



# PYROXYLIN ENAMELS AND LACQUERS

*Their Raw Materials, Manufacture and Application*

BY

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**SECOND EDITION—ENLARGED**

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## PREFACE TO THE SECOND EDITION

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The welcome that the first edition of this book received, surprising and gratifying as it is, indicates most clearly how the interest in pyroxylin lacquers has grown in the past two years. The data on production of these materials are also indicative of the rapid advance of pyroxylin finishes and are best shown by government census figures, which have been gathered together by the *American Paint Journal* and other trade periodicals.

These figures show the following huge increases in the production of pyroxylin lacquers and their accompanying thinners:

1919 .....	500,061	gallons
1921 .....	1,409,280	"
1923 .....	3,255,857	"
1925 .....	7,387,506	"
1926 .....	12,980,400	"

Every indication points to 1927 being an even better year for the industry than 1926. The huge growth is due to many different factors: the almost complete adoption of lacquer by the automotive industry; the increase in production of iceless refrigerators, a large percentage of which are lacquer finished; the increasing use of lacquers on railway equipment; and furniture; and last but not least, the great developments in brushing lacquers which have placed them under one label or another in almost every paint and hardware store. Not

only do these go to the householder for use in decorating his floors and furniture, but a very rapidly increasing number of contracting painters are using lacquer in their work—a number that would unquestionably be greatly enlarged if the opposition of painters' unions toward the use of the spray gun and of lacquers in general could be overcome.

Together with this vast increase in production has come the expected number of changes in ingredients, prices, methods of application. To the list of important solvents in the first edition of this book must now be added such newer materials as the important glycol ethers, amyl propionate, butyl lactate, synthetic amyl alcohol (pentasol) and its acetate, ethyl acetyl glycolate, the group of secondary butyl and amyl alcohols and acetates and still newer solvents which are now being experimented with and which to-morrow may have found their place. New pigments, especially whites, yellows and maroons, have been developed and constant research is continuously going on to improve this important class of materials still further. No new plasticisers of importance have as yet appeared, but the field is open and the newcomer is assured of a welcome. At least one promising synthetic resin has appeared, and with its advent the dependency of lacquer upon foreign sources of raw materials has been practically completely eliminated. A marked decline in the price of low-viscosity nitrocellulose has been one of the accelerating influences on the growth of the industry, and it has been accompanied by lower prices in general for other essential raw materials, and has resulted in rather drastic reductions in prices of finished lacquers. Prices in 1927 for automobile enamels, furniture lacquer, plater's lacquers, etc., are surprisingly lower than in previous years, and as a matter of fact, the bulk of lacquer products to-day are being sold at a considerably lower margin than varnish materials. This has been reflected in the lower earnings of such companies whose overhead is high, and who must either cut quality or profits to compete with the more aggressive low-overhead companies.

In finishing methods we have a variety of new spray guns with improved adaptability to lacquer. Dipping is being resorted to more generally, and flocoting, flowing on the lacquer from a wide nozzle, is being carefully tested by various automobile manufacturers. Undercoats and primers have been improved. Flat lacquers have eliminated rubbing to a great extent, and rubbing machines have supplanted hand-rubbing where flat lacquers have not been found suitable.

The varnish industry has awakened to the menace of pyroxylin finishes: the majority of varnish makers have already entered the lacquer field, and by the use of new resins, wood and perilla oils, and new driers have also produced varnishes and enamels that dry in a very few hours with a fair approximation to a lacquer finish. Some companies are combining lacquer and varnish so as to get a material with the quick-drying qualities of the former and the building properties of the latter. The durability of these hybrids is still uncertain, but some such combination may indubitably be discovered that will be successful.

The writer's apologies are due readers of previous editions for sundry errors therein. Most of these were due to the vague and inaccurate statements in the literature to which access was possible, and many of them have been corrected by authorities who have read this book. The writer believes that more may be found and hereby expresses his hope that anyone who finds a dubious statement will communicate with him. It is only by such errors and corrections that true values can be brought out of authoritative files.

S. P. W.

CLEVELAND, OHIO,  
July 1, 1927



## PREFACE

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In the last few years an almost revolutionary change in the art of finishing metal and wood surfaces has been taking place, and now even the proverbial "man in the street" has added to his vocabulary, hitherto limited to paint, varnish, shellac and japan, the word "lacquer." Probably the largest single factor in this rapid spread of knowledge and use of pyroxylin lacquers and enamels has been their successful application to automobile bodies where under a variety of trade-names such as Duco, Lacqueroid and Zapon they have become familiar to that very high percentage of the American public which is interested in automobiles.

This successful development has been due to several recent and important improvements in the manufacture of pyroxylin, its solvents and its plasticisers and has been concomitant with a tremendous increase in the amount of pyroxylin materials sold and in the number of firms manufacturing them. As a matter of protection, most of the old-line paint and varnish houses have begun to add a variety of these pyroxylin products to their list, often without adequate preliminary experimentation, and a few of them have carried these products to an extent where they rival the previous oleoresinous material in volume and extent. Moreover, a large number of new manufacturers, some fairly large but most of them small, have appeared, and the field is being intensively cultivated under a competition that makes care in production and economy of formula of paramount importance.

As was to be expected, the rise of pyroxylin to a high position in industrial chemistry has caused much activity among manufacturers of allied products. There has been a period of intense research on solvents, resins, plasticisers and pigments, as well as on pyroxylin itself, and this has resulted in the addition to industrial chemistry of many new compounds which were laboratory curiosities but are now bulk chemicals. And the end has not come. The future will undoubtedly see staggering changes in the nature and prices of the ingredients of pyroxylin lacquers.

Manufacturers of these products, as well as chemists and engineers in the pyroxylin lacquer field and production officials of companies which use large quantities of the material have been handicapped by the lack of up-to-date information on the subject. This may seem a surprising statement in view of the fact that in Worden's lexicon on the Nitrocellulose Industry we have as encyclopaedic a book on the subject as almost any branch of industry possesses. But the industry has changed so much since 1911, in materials used and in methods of application, that its present value as a complete reference is reduced by its unavoidable omissions. There seems to be a field for a modest supplementary handbook limiting itself to a concise description of present-day lacquer and enamel practice which may serve as a guide to technical and non-technical reader alike.

No attempt has been made in this volume to be encyclopaedic. It deals only with the materials and manufacture of pyroxylin solutions and with their applications in industry. The celluloid and film industries are not dealt with, as they are adequately taken up in Worden's book. Cellulose esters other than the nitrate are not considered in this book, primarily because they are at present of very subordinate importance in the industry, despite the local importance of viscose silk and cellulose acetate airplane dopes and insulating varnishes. Smokeless powder and gun-cotton, while they are also basically pyroxylin compounds, are not touched upon,

and the book is confined to bronzing liquids, leather dopes, wood and metal lacquers and enamels.

It is the writer's belief that the future of the pyroxylin lacquer industries lies not so much in the so-called secret formulae which in their essentials are known or obtainable to most manufacturers, but in systematic co-operative research toward the standardization and improvement of the products and of plant technique so as to secure a lower cost of production and selling and a greater uniformity of product than is now the case.

In this book a number of formulae are given, most of which have stood the test of sale and re-order. No claim is made that they are the best on the market, and it is impractical to give formulae with any sweeping guarantee when new materials are constantly appearing that may revolutionize all practice. That they are in accord with present-day practice is confidently asserted, but local conditions of competition, weather, idiosyncrasies of material to be finished and of finishing foremen may require radical changes in formulae.

No formula, however, is as important as the one, Care + Honesty + Research = Successful Lacquer. The varnish-maker, with his troublesome and tricky fusions of gums, solution of the melt, clarification and blending, has learned this formula. The lacquer manufacturer, presuming on the comparative simplicity of manufacture, has not always heeded it, but it is safe to assume that those still in the business five years hence will be those who have. To buy a formula, shop around for the cheapest materials, make up a lacquer in a hurry without chemical control and sell it "at a price" may bring volume business for a while, but the eventual downfall is certain.

In preparing this book much helpful information has been obtained from various prime sources of raw material, and the author wishes to express his thanks to Mr. Mueller of the Commercial Solvents Co., Mr. Atwood of the U. S. Industrial

**PREFACE**

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July 30, 1925.



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# PYROXYLIN, ENAMELS, AND LACQUERS

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## PART ONE

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### CHAPTER I

#### INTRODUCTION

The word "lacquer" is derived from the Hindustani "lakh," which means "a hundred thousand." Originally given because of the myriads of insects whose waxy, resinous secretion is the basis of the shellac of commerce, the name bids fair to justify itself in the almost innumerable uses to which the modern derivatives of the old spirit lacquers have been applied. Lacquering, in the generic sense of applying a protective or ornamental finish to articles of wood, metal or fiber, is not new: for centuries the art has been carried on, to a remarkable degree of virtuosity, in China, Japan, Burma, and other Asiatic countries. But, despite the fact that the beauty and durability of this finish are undeniable, the amount of time and painstaking labor required makes the use of Japanese or Chinese lacquer, a natural tree sap of remarkable characteristics, inadmissible for the mass production of Occidental countries.

For this purpose, till comparatively recently, the spirit varnishes or lacquers held sway. These were solutions of various gums and resins in an alcohol, generally denatured spirits or wood alcohol. Shellac was, and is, the preferred resin, but its price led to the use of inferior gums such as rosin, copal or dammar. These spirit lacquers had some valuable properties,

particularly those of quick drying and cheapness, and were soon used in large quantities as protective coatings for metal, where a thin film of clear resin served to protect brass or silver from the action of the elements; for wood, where either as clear solutions or as pigmented spirit enamels they supplanted the slow drying varnishes and varnish enamels for work where high speed of production made a quick drying finish necessary; and as protective, stiffening, and ornamental agents for leather, paper, plaster of paris and in fact almost any conceivable material.

Even the best of these lacquers, however, had indubitable faults. They had a tendency to soften in warm weather, and to crack in cold. The film lacked resistance to abrasion and to the destructive action of the sun's rays. Water was apt to whiten and ruin the finish. They were not entirely satisfactory but the best that technology offered at the time.

Contemporaneous with the rise of spirit lacquers was the much slower growth of pyroxylin solutions. Solutions of this partially nitrated cotton in ether-alcohol mixtures had found early use in photography, wherein they served to prepare the collodion plates, and in medicine where the tough residual film offered a convenient protection for small cuts and scratches. For other purposes, however, the low boiling solvents, the only ones then available, were inadequate. Their rapid evaporation lowered the temperature about the liquid to a point where atmospheric moisture condensed and precipitated the pyroxylin as a whitish, opaque film of low tensile strength. The discovery of celluloid, moreover, withdrew much of the interest in liquid pyroxylin solutions and focused the inventive spirit in the field on the solid solutions of pyroxylin with camphor and its substitutes.

In 1882, however, J. Stevens patented the use of amyl acetate as a solvent for pyroxylin and thus laid the foundations for what is to-day one of the most rapidly growing fields of chemical industry. This solvent permitted the deposition from solution of a hard, transparent lustrous film of great durabil-

ity. At that time, the available pyroxylin, when dissolved in amyl acetate, gave a solution of very high viscosity even at concentrations as low as 6 ounces to the gallon. This limited the application of pyroxylin lacquers to those purposes where a thin film was desired, particularly to the protection of brass and silver articles where it has practically replaced the shellac lacquers. The invention of artificial leather, which is essentially a cheap fabric coated with pyroxylin solution and then embossed to show a grain, followed, and provided what is even now one of the largest outlets for pyroxylin solutions. Under the name of "leather dopes" tremendous quantities of pyroxylin solutions are sold annually to the manufacturers of artificial leather, and also to those making patent leather.

This use created a growing demand for amyl acetate, and the fusel oil from which it is derived. Fusel oil, a by-product of alcohol manufacture, had been of so little value that peasants in Russia, Hungary and other countries used it as an illuminant. Now its price increased by leaps and bounds, distilleries that had formerly allowed it to run to waste set about recovering it, and still the demand remained unsatisfied and the price rose continuously. Chemists began systematic research on possible syntheses of the material and on the increase of the yield of fusel oil in the fermentation of carbohydrate-containing material. The synthetic methods have fallen short of commercial success, although two of them showed excellent promise in the laboratory stage. These were the hydration of unsaturated hydrocarbons produced in the cracking of petroleum, with subsequent acetalation of the isoamyl alcohol thus produced; and the chlorination of the pentane fraction of natural gas followed by treatment with sodium acetate solution, thus obtaining amyl acetate without going through the amyl alcohol, or fusel oil, synthesis.

The study of fermentation possibilities, however, was more successful. Ehrlich discovered that the fusel oil was

N. B.—However, in 1927 commercial production on a large scale of synthetic amyl alcohol and amyl acetate, under the names of Pentasol and Pent-Acetate, was achieved. Details will be found in the chapter on Solvents.

produced by the fermentation of the amino acids in the grain, and not from the carbohydrates. Then came the Fernbach process, wherein a specially cultivated bacillus was found to produce a high percentage of fusel oil in the form of amyl and butyl alcohols. High hopes were held for this process, which promised to solve not only the fusel oil problem, but also that of synthetic rubber. For some technical or economic reason the Fernbach process was never an industrial success, but it paved the way for the Weizmann process, which more than any single factor has led to the vast expansion of the pyroxylin lacquer industry.

The essential difference between these two processes lies in the fermenting agent, the successful Weizmann agent being the *Bacillus granulobacter*. By the latter method, more fully described under butyl alcohol in Chapter III, corn is made into a mash, sterilized, inoculated with a culture of the proper bacillus, fermented and distilled. A very high yield of a mixture of acetone and butyl alcohol is obtained and it is this butyl alcohol and the butyl acetate made therefrom that have made it economically possible for lacquers and enamels to be made that can compete with varnish and varnish enamels as well as with shellac solutions. Till recently the manufacture of butyl alcohol was a close monopoly. The company operating under the Weizmann patents originally adopted the process for making acetone, for which during the war there was a great demand. When peace was declared, butyl alcohol became the prime product and acetone a by-product. During 1922 and 1923, this plant was practically forced to suspend operations, owing to a great reduction in the yield through some very difficultly traceable cause. Much research has been devoted to the problem and under present conditions of sterilization and other control the company's plants in the Indiana-Illinois corn belt are producing tremendous quantities of very high-grade product at a price which fluctuates with the changes in the corn market but is always under that of amyl alcohol or fusel oil. Very recently, German butanol synthesized

from acetylene, has appeared in quantity at the New York market and is competing with the domestic product. Other interests are reported as planning to enter the field, and any danger of a monopoly of this material seems to be past.

The price of butanol, of course, is connected closely with that of the by-product, acetone. This had heretofore been a product of hardwood distillation, along with wood alcohol, charcoal, methyl acetone and acetone oils. The accumulation of huge acetone stocks by the butanol producers led to a trade war in which the price of the product has been cut nearly in half, and the wood distillers placed in a position where the subsequent announcement of synthetic wood alcohol from Germany seems to sound the death-knell of the industry. Acetone itself is of minor importance in the lacquer solvent industry, but certain derivatives such as diacetone alcohol and mesityl oxide seem to promise an extension of its use.

Cheap butanol, which means the possibility of making cheap butyl acetate having been achieved, a further step was needed before the pyroxylin lacquer industry could reach its full growth. This was a method of securing a solution containing a high percentage of solid matter and yet not so viscous as to permit of application by the spray-gun. The old-time pyroxylin could scarcely be dissolved to four ounces to a gallon without attaining too high a viscosity for proper spraying and this compared very unfavorably with the 2 to 4 pounds of shellac or its substitutes and the much greater weight of oil varnish and enamels that is contained in a gallon of the material. The art of the cotton nitrator was called into play and the result was the perfection of low-viscosity pyroxylin, a product which gives a solution of about 1/50 of the viscosity of the old-time pyroxylin. Gums or resins of various types can be added to this solution without perceptibly increasing the viscosity. Present high-grade lacquers contain about 24 ounces of pyroxylin and 16 ounces of gum to the gallon, giving a total film weight of  $2\frac{1}{2}$  pounds to the gallon.

With the new solvents and new nitrated cotton, the real inroads of the pyroxylin solutions on the strongholds of the paint and varnish industry began. The automobile proved to be first to capitulate, and the last two years have seen a majority of the car manufacturers abandoning their baked enamel or slow-drying varnish enamel finishes for the incomparably simpler, more durable, harder lacquer finishes. Hundreds of re-finishing stations have also adopted this material for similar reasons. A competent spray man can be trained in a tithe of the time required for the education of a good brush painter, and can do far more in a given period. A car can be completely finished in two days or even less, thus effecting a substantial saving in overhead. This is more illuminating when it is considered that a good paint job formerly required from one week to nearly a month to complete, and the car was occupying space in the shop and collecting a portion of the rental overhead throughout that period. When properly applied, lacquer finishes have been known to last as long as three years without cracking, alligatoring, chalking or otherwise depreciating. Only by use of the most expensive materials, and the most expert labor could the previous finishes approach such a record. Lacquer finishes are proof against battery acid, gasoline, alcohol, water and abrasion due to the rubbing off of dried mud and grit. In one respect, however, they are inferior to previous finishes, namely in degree of gloss. The luster of lacquer finishes corresponds to that of satin, and although a higher gloss can be obtained by the use of higher percentages of gum with the pyroxylin, such a coating lacks the durability of the satin finish. Attempts have been made, with some success, to use a high gloss finishing varnish on top of pyroxylin enamels, but in general the lacquer makers have attacked this problem by the simple method of making the satin finish popular through judicious advertising. As counterbalancing features they offer a much wider choice of colors than heretofore obtained, and a finish whose luster, instead of depreciating with age, actually in-

creases with the number of times it is washed and wiped off.

The furniture industry was next attacked, and progress here, while much slower, proved by the steady increase in the numbers of users that the time will soon come when this field also will be pre-eminently occupied by pyroxylin lacquers and enamels. Many of the steel office furniture makers have adopted this finish instead of the baked enamel previously used, and thus avoid the cumbersome baking ovens, the extra labor and the time required for conveying the furniture to and from the ovens and in the baking and cooling processes involved. Much of the enameled wood furniture of the better type is to-day made with pyroxylin, and as formulae are simplified to lower the cost, more and more of it will be treated by this incomparably more rapid, more durable and more beautiful finish. In the radio cabinet field, lacquer has found an excellent reception, as its slightly higher cost has been found more than counterbalanced by the increased speed and economy of application, as well as the superior qualities of the finish. The makers of the finest type of furniture, such as pianos, are more hesitant, as they are not certain of the durability of lacquer finishes over very long periods. Experiments are being constantly carried on, however, and it is not too much to hope that even the ultra-conservative piano manufacturers will eventually come to pyroxylin as against the time-consuming, laborious, expensive varnish finishes now employed.\* On the other hand, the manufacturers of the very cheap furniture, who now use shellac or a so-called varnish that costs a mere fraction of that used by the piano industry, need only a lowering of price to bring them within the pyroxylin fold. It can safely be said that where a combination of high daily production and high quality of finish is required, pyroxylin lacquers and enamels can even to-day compete successfully with any other finish.

\* N. B.—A very large proportion of walnut pianos are now finished in lacquer, although only a small percentage of the mahogany pianos are produced in this finish.

In the last few years a third field for lacquers has been opened up, and one which may in volume of material used exceed any of those previously described. This is the field of interior decoration, particularly of hotels, office buildings and apartment houses. At first glance the high cost of lacquers compared to paint would seem an insuperable obstacle, but the fact remains that many such buildings have been decorated by pyroxylin enamels. The speed of application and drying is the salient point here, for not only is there a marked saving in the time and consequent labor cost in the operation, but the building is ready for occupancy one or two days earlier than otherwise possible. It can readily be calculated that a hotel of a thousand rooms can well afford a small extra material cost if one day's use of these rooms is gained thereby.

Of the innumerable minor uses of lacquers and enamels with a pyroxylin base only a few can be mentioned here. The objects finished thereby range from collar-buttons to airplanes, and include articles of wood, glass, steel, brass, silver, nickel, aluminium and white metal. Large quantities are used by electro-platers as a protective coat for their products after plating and burnishing. Even larger amounts are consumed by the spun brass manufacturers, such as the makers of lighting fixtures, vanity cases, mirror and brush handles, etc. The toy and doll industries are large users, as are the makers of lead pencils and broom handles, who, by the way almost invariably dip their product instead of spraying. Other users will be mentioned throughout this volume, but enough has been said to demonstrate the diversified and extensive applications of pyroxylin solutions.

The question naturally arises, "What bearing will this have on the varnish manufacturers?" The answer is simple. They are now, almost without exception, making lacquers, and while it must be admitted that their pyroxylin products are not generally of the same quality as their oil varnishes, due to their recent development, their research staffs are constantly bettering the quality and it will be only a short while

## INTRODUCTION

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before they are offering a pyroxylin product with the ~~SINGAPORE~~ confidence and guarantees they now hold forth for their other items. Moreover, there are many uses for paint and varnish for which even the most ardent protagonists of pyroxylin see small hope of replacing. These are the house paints, railroad and steamship paints, and the paints, varnishes and enamels sold in cans to householders for application with a brush. The necessity of a spray gun, with its attendant paraphernalia of air-compressor, pressure tank, gauges, etc., practically restricts the use of pyroxylin to the factory and the large contractors with portable equipment. Considerable work is now being done on brush lacquers and enamels, i.e., pyroxylin solutions containing solvent of high enough boiling point to permit of the material being applied with a brush without showing brush marks, and yet drying quickly enough to partake of the advantages of a sprayed lacquer. Several million gallons of brushing lacquers have been sold to the public in the last two years and a definite place in the field has been attained. There is room for much improvement in these lacquers, but their unquestionable advantages have almost eliminated the slower drying varnish enamels previously used.

Some interesting economic problems are connected with this encroachment of pyroxylin upon oil and resin finishes. In the first place, the varnish industry has long been concerned over the growing scarcity of high-grade fossil resins, such as Animi and Kauri. Synthetic resins have fallen far short of the required quality, as have the more recent copals from natural sources. It is understood that extinction of the New Zealand Kauri supply is only a matter of a few years and even to-day gross adulteration with inferior resins is being practiced. Cotton, on the other hand, is a yearly crop, sulphuric and nitric acids can be produced to any desired extent, and the solvents are products of fermentation of natural grains and sugars. In other words pyroxylin and its solvents may be considered inexhaustible.

The decrease in demand for linseed oil resulting from a continual replacement of varnish by pyroxylin will necessi-

tate either a reduction of the crop, or some other outlet such as edible hydrogenated oil. No drastic measure seems necessary, as linoleum and paints will continue to require their enormous annual quantities.

Turpentine is used in large quantities in paints and varnishes and practically not at all in lacquers. Any decrease in demand for turpentine, however, will be offset, as far as the producers are concerned, by the increased use of rosin, which when esterified with glycerin, provides the ester gum that is used throughout the lacquer industry.

Other changes in the economic structure will undoubtedly result as new products are developed for use in this field and the whole chemical industry will in all probability be affected by the Gargantuan growth of this lusty infant.

## CHAPTER II

### **PYROXYLIN**

By treating cellulosic material, such as paper, wood-pulp or cotton with nitric and sulfuric acids a series of compounds are produced which are broadly and incorrectly termed nitro-celluloses. They are really cellulose nitrates, and their true constitution is being unraveled as the complex cellulose molecule itself gradually yields to the brilliant researches which are constantly being carried on. There is no space in this volume for an extended study of the chemistry of cellulose and the reader is referred to Worden and to the books on the subject by Hall and Heuser, West and Esselen for a survey of the progress made in recent years. For practical purposes, cellulose may be considered as a complex alcohol, with three hydroxyl groups for each unit molecule. These alcoholic radicals can be esterified by acids and the acetic and nitric acid esters have tremendous importance in industry.

Gun-cotton is a nitro-cellulose of maximum degree of nitration, containing over 12.5 per cent of nitrogen. This is practically insoluble in the materials used in lacquers and therefore useless except for explosives. The pyroxylin of the lacquer and celluloid industries is not a chemical individual, but a series or blend of nitro-celluloses containing from 11-12.5 per cent of nitrogen, and often some oxy- or hydro-cellulose and their nitrates. Poorly made grades may contain a very high percentage of these latter substances, which are unstable, of poor tensile strength and generally undesirable. They are most likely to occur in the low-viscosity pyroxylins, where the conditions of manufacture favor the

breaking down of the cellulose molecule to these degradation products. In properly made pyroxylin, even of low viscosity, these impurities are reduced to a minimum, although it is generally conceded by the trade that there is greater strength and durability to the high viscosity pyroxylin.

### Manufacture of Pyroxylin.

The raw materials in this country are almost exclusively cotton linters and very high grade tissue paper. The latter is used in comparatively small quantity for certain special purposes where a practically colorless material is desired, but linters are the source of the vast bulk of the pyroxylin products made and used to-day.

Linters are the short fibers of the cotton plant, left after the larger fibers have been removed for spinning into thread or cloth. Their value is proportionate to their distance from the seed, the poorest quality being that immediately enveloping the cotton seed. Cotton mill waste and occasionally, for specially high grades, the long fiber cotton itself have been used. In Germany, during the war, much smokeless powder was made from purified wood pulp, and it is to be hoped and expected that some day waste sawdust will be transformed to pyroxylin economically, although at present the expense of purifying the wood cellulose from its encrusting lignin and of bleaching the fiber makes this impractical.

Linters and mill waste alike require purification before nitration. Not only are mechanical impurities present, but a certain amount of oil is always found in the fiber and this would cause much trouble and danger in the nitrating bath. Purification is usually done by boiling in a solution of caustic-soda under 75-85 pounds pressure. The alkali is washed out carefully and if it is desired to produce a colorless pyroxylin the cotton is next bleached with chloride of lime. After acidifying in another thorough and careful washing the cotton is run through a machine that loosens the matted fibers and

dried to a moisture content of less than  $\frac{1}{2}$  of 1 per cent. If too energetic a purification is given the cotton, such as boiling for too long a time or at too high a temperature, the strength of the resulting pyroxylin will be diminished.

The cotton is weighed into dipping pots, a charge generally consisting of 32 pounds of cotton and about 1600 pounds of mixed sulfuric and nitric acids. The composition of the mixed acid must be very carefully controlled, as slight difference in content of acids, water or nitrogen oxides may appreciably alter the properties of the resulting pyroxylin. A typical mixed acid formula consists of 20 per cent of nitric acid of 1.47 specific gravity, 40 per cent of nitric acid of 1.36 specific gravity and 40 per cent of sulfuric acid of 1.84 specific gravity. Many of the formulae used and a thorough treatment of nitration are to be found in Worden's book.

The temperature of the solution is also of great importance, and on it depends largely the type of pyroxylin produced. Temperatures of 35-55° C. are generally employed. The nitrating pots are usually arranged four to a unit on the third floor of a three-story building. Acid of the proper composition and at the proper temperature is pumped into the pots, which are provided with steam pipes for heating and cold water pipes for cooling if required. Two stirrers are so arranged that the cotton is rapidly submerged and kept in motion through the large excess of acid. The large excess is required to avoid the change in composition of the acid due to the amounts used up in the reaction. In a large amount of acid this change is negligible and the variation in composition of the pyroxylin which would occur if only the calculated amount of acid were used is thereby avoided.

The reaction takes from 15 minutes to 1 hour, depending on the type of pyroxylin desired, the temperature and the acid composition. When completed, the cotton and acid mixture is allowed to fall through a valve in the bottom of the pot into a centrifuge on the floor below. The acid is thus whizzed out in a few minutes, and is pumped back to tanks

where a calculated amount of strong fortifying acids is added to it to bring it back to the desired concentration for re-use. From the centrifuge the cotton is discharged into a bowl where it is submerged in cold water and thence a water stream running through earthenware pipe-line sweeps it into the boiling tubs.

The pyroxylin at this stage contains a certain amount of very undesirable absorbed acid, and some unstable cellulose sulphates and nitrates. By boiling with a slightly acid water these unstable esters are hydrolyzed and some of the absorbed acid removed. Boiling generally requires about 8 hours, though longer periods are required for smokeless powder nitro cellulose.

The matted lumps are next transferred to a pulping machine that beats them up into a short-fibered pulp and thus renders the narrow fibers accessible to the purifying waters in the poaching tubs. In these tubs the pyroxylin is boiled for about 12 hours with 5 changes of slightly alkaline water and then washed with fresh water. Pyroxylin for lacquers is often given a bleaching treatment at this point.

Since it is very difficult, even with the best of control, to keep any individual batch uniform, every effort is made to blend batches to secure an average uniformity. At one plant 33 dipping pot batches are added to 1 boiling tub, then portions of several boiling-tub batches are added to each beater and poacher and finally the contents of several poachers are blended in a large blender to give a very uniform product.

The pyroxylin is now pure, except for the presence of about 25 per cent of water. This is undesirable for the manufacture of lacquers, as water is a precipitating agent for pyroxylin. On the other hand, dry nitrocellulose is a very dangerous substance and its transportation is forbidden by common sense as well as by the Interstate Commerce Commission. Therefore, practically all of the commercial pyroxylin is dehydrated by forcing denatured alcohol under 300 pounds pressure through the wet cotton, and the product as

sold contains 30 per cent of denatured alcohol by weight. Since alcohol mixes well with most ingredients of a lacquer formula, and since it is used to a large extent therein, this is not a deleterious ingredient, and is acceptable as a moistening agent to reduce the danger of handling and transporting the material.

### Viscosity.

For a long time the only available pyroxylins gave solutions that were very thick and viscous even in concentrations of a few ounces to a gallon. This restricted their use greatly and much effort has been spent on ways to reduce this viscosity and at the same time retain the desired properties of the material. It was found possible to reduce viscosity by regulating the temperature, composition of acid and time of reaction. A higher temperature, lower concentration of nitric acid and shorter reaction period all favored a reduction in viscosity. Unfortunately, they also favored a reduction in yield and had a tendency to form undesirable oxy- and hydro-celluloses.

A more practical procedure consists in first obtaining a pyroxylin of high viscosity, and then boiling under high pressure. This reduces the viscosity without seriously affecting the strength of the material. A cheaper and more rapid method was discovered wherein a pyroxylin solution was warmed with  $\frac{1}{2}$  of 1 per cent of pyridine, or similar amine. This gives a product of low viscosity, but of poor quality, as the action of the pyridine seems progressive and results in rapid decomposition of the film. Recently an attempt has been made to prepare a low-viscosity pyroxylin from salvaged smokeless powder by similar methods but it is scarcely to be recommended for any goods of high quality. Cases are reported where this type of material has apparently flared up spontaneously.

A method described in British Patent 136,141—1917 claims that viscosity of pyroxylin solutions can be reduced by heat-

ing to 60° C. or higher in closed containers. It is claimed that such methods are being employed in this country, the drums containing the solutions being placed in a room heated to the desired temperature and kept there the requisite length of time. Naturally drums of a capacity sufficient to take care of the thermal expansion of the contents are used.

Another suggested method claims the use of ultra violet rays as a means of reducing viscosity. Since it has been well proved that ultra violet rays are among the most potent factors in breaking down pyroxylin films it is scarcely possible that this reduction in viscosity does not imply a serious deterioration in quality of the product.

The question of viscosity of pyroxylin solutions is a most important and most vexing one. It is generally agreed that they are not true solutions, but plastic masses, and subject to so many variables that few valuable generalizations can be made. It was once thought that the viscosity was correlative with the nitrogen content, but this has been disproved. It certainly depends on the solvent, for solutions of equal concentrations in acetone or ethyl acetate are less viscous than those in amyl acetate. Addition of non-solvent increases the viscosity. Increase of concentration does not give a proportional increase in viscosity, except in low concentrations of low-viscosity pyroxylin where it does so approximately. Viscosity decreases with rise in temperature, in conformity with a general rule, but here again there is no mathematical relationship.

It is most important that lacquer solutions have uniform viscosity, for the technique of application, such as thinning and spreading or spraying, is based on a definite standard and a variable viscosity would introduce too many plant complications. Several means of determining viscosity have been developed and in proper plant practice are constantly used in checking and rechecking the produce.

The falling ball method is the simplest and most widely used method. It depends on the resistance to the fall of a

standard ball of a definite column of solution. For testing pyroxylin, a solution of the material in acetone was used, but since this gives lower viscosities than the average lacquer composition actually made in the plant, a mixture of ethyl acetate, ethyl alcohol and benzol has been adopted as the standard solvent by the Hercules Powder Company, one of the largest factors in supplying pyroxylin. They prescribe a solution made by adding to 12.2 parts by weight of the pyroxylin, 22 parts of 95 per cent denatured alcohol, 48.3 parts of 90° benzol and after shaking adding 17.5 parts of 99 per cent ethyl acetate and again shaking till thoroughly dissolved. This corresponds to a 16 ounce per gallon solution.

A glass tube 14 inches long and 1 inch in diameter is used. A rubber stopper is inserted in the lower end, and two file-marks made 2 inches from each end. The solution is brought to 25° C. and poured into the tube. A steel ball-bearing  $\frac{5}{16}$  inch in diameter and weighing 2.043 grams is dropped into the liquid after being previously moistened with the solvent used above, and the time required for it to traverse the 10-inch column of liquid noted on a stop-watch.

The commercial pyroxylins require from 200 seconds to  $\frac{1}{2}$  second under these conditions. Bronzing liquid cotton of a nitrogen content just below 12 per cent and so purified as to be compatible with bronze powders has a viscosity of about 40 seconds. Pyroxylin for leather dope is generally of 30 to 40 seconds, although for some special types a 100-second cotton has been used. Metal lacquers usually take the 60- to 80-second type. For cheaper enamels a 4- to 10-second pyroxylin has received considerable favor while the high-grade enamels and wood lacquers use the  $\frac{1}{2}$ -second type in very large amounts.

Several difficulties are found in the falling-ball method. It is hard to keep the temperature constant, and a slight temperature change alters the viscosity greatly. In thin solutions the speed of fall is so great that accurate measurement

is very difficult. Moreover, for highly colored lacquers and for enamels the method is obviously unsuited. The Stormer, Ford and MacMichael viscosimeters are called for under these conditions, and are described in Chapter XII.

The subject of viscosity merits further discussion. By the method above we have determined that the solution, containing 16 ounces pyroxylin to a gallon of acetone, has a viscosity of, say, 20 seconds. This does not mean that this same cotton dissolved in any other solvent will have the same viscosity. On the contrary, if the second liquid be a poorer solvent, the viscosity will be greater; if a better solvent it will be less than in acetone. Neither does it follow that a 32-ounce solution in acetone will be of 40-second viscosity, because although for dilute solutions increase in concentration means a proportionate increase in viscosity, for each combination of pyroxylin and solvent a point is reached at which a further increase in concentration of pyroxylin leads to a disproportionate thickening of the solution. What the viscosity determination actually tells us is that if the formula calls for 1 pound of 20-second pyroxylin, the above material will be satisfactory for the purpose.

As mentioned previously, the low viscosity cotton is the basis of the present wood lacquers and lacquer enamels of the better grade, wherein actual body is of importance. However, in bronzing liquids wherein only a few ounces of pyroxylin are used, it is of importance to use the high-viscosity material, for although the others would have equal body they would be too thin to suspend the bronze powder properly. Moreover, many of the users of bronzing liquids, as well as the cheaper enamels, have become accustomed to material of high viscosity, which they miscall high body, and are chary of accepting a product of lesser thickness even if it contains more actual solids per gallon. It has always seemed advisable to the author to bring up the viscosity of these products by the judicious blending of cottons of different viscosities, 40-second cotton for its thickening effect and the others for ac-

tual solid content. The viscosity of a given solution may be increased by the addition of a non-solvent, such as benzol, almost to the point of precipitation; and conversely, a too thick solution can be thinned markedly by the addition of small percentages of acetone or ethyl acetate. A point to be remembered is that most users of pyroxylin prefer to get a product which they can thin or dilute with an equal part of the cheaper thinner that accompanies all pyroxylin products. Consequently, the original bronzing liquid, metal lacquer or enamel is made rather thick, except in the automobile or similar high-grade lacquers and enamels where high actual solid content is an important desideratum.

### Properties

The pyroxylin as it comes in the trade resembles cotton waste in its appearance but possesses a slightly harsher feel. It has the odor of the alcohol with which it is moistened, and while readily inflammable is not explosive. The true specific gravity of pyroxylin is about 1.6, but the commercial material is so porous that its apparent specific gravity is very much less. When dissolved in an appropriate solvent and allowed to dry, a clear transparent film results, of exceptional hardness and great durability. If the solvent is very volatile and the air humid, the rapid evaporation cools the air about the film to below the dew point and the condensing moisture whitens and opacifies the film. This is commonly termed "blushing" and is the bane of the lacquer maker and user. A pyroxylin solution has to a pronounced degree the property of contracting on drying, and this not only causes wrinkles or ridges in the film but causes it to buckle or "bridge" away from the surface to which it has been applied. For these reasons it is very important to use the right plasticiser, in a proportion sufficient to prevent this contraction but not so great as to sacrifice the valuable hardness of the film. This is of especial importance in enamels, where the added pigment increases greatly the brittleness of the film.

From its mode of manufacture pyroxylin might be expected to be very resistant to acids, and the expectation is justified by experience. It is used therefore as a covering for battery separators or electrolytic diaphragms where acid conditions are encountered. Pyroxylin is resistant to water, hot or cold, although unplasticised films containing no resin are easily stripped from glass or metal by hot water. Pure alcohol generally has no effect, although certain types of pyroxylin have been prepared which are quite soluble in absolute alcohol. Denatured alcohols may have a solvent effect owing to denaturants such as commercial wood alcohol which contains acetone. Gasoline or carbon tetrachloride have no effect on pyroxylin.

Alkalies act on it, in proportion to their concentration and temperature, saponifying cellulose esters as they do fats, but with much greater difficulty. Ammonium sulfide reacts vigorously on pyroxylin, decomposing it rapidly.

Sunlight and ultra-violet light have been found to cause deterioration of pyroxylin, as well as of all other finishes. This actinic decomposition is greatly lessened by the presence of opaque pigments, which apparently absorb the harmful ultra-violet rays, and thus pyroxylin enamels on automobiles have stood up for years exposed to sun and rain.

A thin film of pyroxylin does not possess a high gloss and where this is desired resins and oils are incorporated into the mixture.

### Acidity.

Pyroxylin may contain some residual acid, and pyroxylin solutions may be acid either from this cause or from the solvents employed. Such acidity is in general undesirable, and particularly so where the material is to be used on metal, such as copper or brass. It is generally tested for by evaporating 25 to 50 c.c. of the material in a bright copper dish over a steam bath. If a green color appears the material is too acid.

A brown color sometimes appears where alkali has been left in the pyroxylin, but this is a very unusual occurrence.

A quantitative determination can be made by adding to a weighed sample of solution double its volume of a 50-50 mixture of alcohol and water, previously neutralized. More alcohol is then added until all the pyroxylin is precipitated. The supernatant liquid is decanted off, the pyroxylin washed with more alcohol, and the combined liquids titrated with tenth-normal sodium hydroxide solution, using phenolphthalein as indicator. The acidity, calculated as acetic acid, should not be greater than 0.1 per cent.

### Color.

The very best pyroxylin gives a practically colorless film. Commercial varieties run from very light yellow to orange-red. Specifications for purchase should be drawn to cover this, for although it is at present impossible to secure uniformly water white solutions, there is no excuse for the deep yellow and red colors that make the product unutilizable on silver and brass and even injure the color of white enamels. Some makers have tried to mask this by adding such dyes as methylene blue, but this is a practice to be condemned, and if the pyroxylin makers are held to a definite color standard it will be unnecessary.

Colors can be matched according to the Gardner-Holdt method, whereby solutions of caramel in water, sterilized by traces of salicylic acid, are made up into a series of faint yellow to dark brown standards. These are kept in tubes of uniform size and shape and a solution of the unknown product in a similar tube can readily be matched against these standards.

### General Discussion.

The making of nitro-cellulose is not a very complicated process, and the basic knowledge is easily accessible. How-

ever, the expense of plant required, the fire and the explosion hazard, and the careful control necessary to produce the material efficiently and uniformly, have led even the large users of pyroxylin in lacquer manufacture to buy their material from established houses rather than make their own. One or two companies, notably E. I. Dupont de Nemours and Co., make pyroxlyn and lacquers and enamels therefrom. This company together with the Hercules Powder Company have acquired great skill in the manufacture of nitrocellulose in their manufacture of guncotton, smokeless powder and similar explosives, and have turned their skill to good account in making lacquer pyroxylin. The Hercules Powder Company does not make lacquers, but is probably the largest purveyor of pyroxylin to the trade. Several smaller companies make their own pyroxylin, but are gradually finding it advisable to purchase it from the specialists in the field.

In small quantities pyroxylin is shipped in iron milk-cans; in larger quantities in wood or steel open head drums holding about 100 pounds. Since it is generally made into lacquers rapidly, there is not the problem of decomposition on storage that is encountered in smokeless powder, but preservatives such as urea or diphenylamine are often used in both the pyroxylin and in its solutions. The function of these materials is to combine with traces of nitric oxides liberated in decomposition, and thus prevent the autocatalytic effect of their presence and accumulation.

### **Expansion on Solution.**

When pyroxylin is dissolved, there is a certain expansion in volume. The available data on the actual numerical value of this important factor are confusing. For each four ounces of dry pyroxylin dissolved in a gallon of solvent values of from 2.5 to 5 per cent increase in bulk are given. There are several reasons for this uncertainty, inasmuch as the value

depends on the type and viscosity of the pyroxylin on the nature of the solvent and on the total concentration. As the material becomes more and more viscous there is a lessening of the increase of volume for added increments of pyroxylin. The writer has found an average of 3.0 per cent increase in volume for 4-ounce increments up to 12 ounces, about 2.5 percent from 12 to 16 and lower values for more concentrated solutions. It would appear to be well worth while for a comprehensive study of the change in volume with concentration to be made, with a variety of typical solvents and a number of different pyroxylins. This might give some insight into the actual physico-chemical condition of the pyroxylin "solutions."

If we assume the specific gravity of pyroxylin to be 1.6, and that of denatured alcohol as 0.80, the specific gravity of commercial pyroxylin will be 1.36. The theoretical bulking value, in a solution of specific gravity of 7.5, would be 10.2 pounds to a gallon, giving an expansion of about 2.4 per cent for each four ounces of commercial pyroxylin. This would hold true if the pyroxylin were inert and insoluble, but so many other factors enter in that this is only an approximation.

The Hercules Powder Co., after a careful study, has found that for a solution of  $\frac{1}{2}$ -second cotton in a solvent consisting of equal parts of toluol and butyl acetate, the bulking value per pound of wet cotton is 0.0937 gallon, or very close to  $10\frac{3}{4}$  pounds per gallon. Solvent mixtures of different density will naturally give different values.

Many lacquer makers buy their pyroxylin already dissolved in some specified solvent, and on a basis of so many ounces to a gallon. It is necessary to know the expansion to calculate the actual amount present in a gallon, so it is more reasonable to demand so many ounces of dry pyroxylin *in a gallon*. If a solution is bought containing, let us say, 16 ounces wet pyroxylin to a gallon, it will be found that taking expansion and alcohol percentage into account we have actu-

ally only 10 ounces of pyroxylin in a gallon of solution. A common procedure for suppliers of these solutions is to charge the market price for pyroxylin and for the solvents, taking the expansion on mixing as their profit, after deducting the expense of dissolving, filtering and shipping.

## CHAPTER III

### SOLVENTS

It must be clearly understood that the solubility of pyroxylin in a solvent is not the same thing as the solubility of salt in water. The latter is a true solution, reaching a definite value in a given solvent at a given temperature. The former is a colloidal solution, similar in many ways to a jelly, which possesses no definite saturation point. In a given solvent, pyroxylin may be dissolved almost indefinitely, although the solution will soon become a thick, viscous gel. The definition of a good pyroxylin solvent, then, is one that will hold a large amount of the pyroxylin and still retain a manageable fluidity. By far the most important group of solvents is that known as esters, or compounds formed by the interaction of alcohols and acids. Since pyroxylin itself is an ester, the general rule that like dissolves like holds true here also.

Of these esters, those formed from aliphatic alcohols, i.e., wood or methyl alcohol, ethyl alcohol, butyl alcohol, amyl alcohol, etc., and acetic acid are of paramount importance. Consideration of these solvents should commence with the alcohols from which they are derived.

### ALCOHOLS

#### Methyl Alcohol—Wood Alcohol—Methanol.

One of the early solvents of pyroxylin was wood alcohol, the volatile solvent produced during the distillation of hard-woods. Most of this solvent power has been traced to the presence of appreciable quantities of acetone and methyl ace-

tate in the crude wood alcohol, but there seems evidence for believing that even pure methanol has some solvent power on pyroxylin, at least to the extent of gelatinizing it. Its chief use in the pyroxylin industry, however, is as a solvent for gums and resins. Until the advent of cheap denatured alcohol, the price of wood alcohol was considerably lower than the heavily taxed ethyl alcohol and it was therefore widely used as a solvent for shellac and similar resins. Its toxic properties were a disadvantage, and denatured alcohol replaced it in large measure. In 1925, however, the synthesis of methanol from carbon monoxide and hydrogen at a cost far below that of the product of wood distillation was announced and thousands of gallons of the material have arrived from Germany to undersell the domestic product. The process is described by Lormand (*Jour. Ind. and Eng. Chem.* 17,430, 1925) and appears very simple. The mixture of gases is passed into a pressure apparatus and the combination of moderate heat, high pressure and the presence of such a catalyst as zinc oxide causes a reaction wherein methanol, higher alcohols and a mixture of hydrocarbons, alcohols, etc., suitable for motor fuel is produced. The producers of butanol are now marketing synthetic methanol derived from the carbon dioxide and hydrogen gases which result as by-products of their fermentation process. If the asserted low cost be true, methanol will undoubtedly undersell even denatured alcohol, over which it has the advantage of being practically water-free. For pyroxylin solutions that are to be sprayed it is doubtful whether its other advantages will outweigh its marked toxicity.

Typical specifications for methyl alcohol are as follows. It must contain at least 97 per cent of alcohol, less than 0.02 per cent of free acid (as acetic acid), be miscible with at least 6 volumes of water and have a specific gravity of 0.799 to 0.805; 90 per cent should boil between 63° and 73° C., with less than 3 per cent boiling above 77° C.

### Ethyl Alcohol.

This compound needs little introduction to the reader: It is one of the longest known and used of all substances, with a pedigree dating back to Noah, and its recent ostensible banishment from the beverage field has only emphasized its importance in the chemical and allied industries. It is the basis of the spirit varnish industry, as the previously used wood alcohol is now both more expensive and more poisonous. The vast celluloid industry uses tremendous quantities, for pyroxylin and camphor, moistened with alcohol, form the plastic mass which heat and pressure transform to this widely used substance. In medicine, perfumes, explosives, as an anti-freeze in automobile radiators, as a source of ethylene, ether, acetaldehyde and scores of other chemical compounds, ethyl alcohol has earned a place as the most important organic chemical.

Pure ethyl alcohol, or ethanol, is to-day a rarity outside of the chemical laboratory, due to the restrictive prohibition laws. Practically all of the alcohol of commerce is denatured with some ingredient that is supposed to make it unfit to drink and yet will not reduce its value for the commercial purpose for which it is purchased. The completely denatured alcohol, containing wood alcohol, benzol and pyridine can be bought without a permit, but this type is not well suited for the purposes of the maker of pyroxylin solvents and solutions owing to the odor, color and comparatively high percentage of denaturants. The preferred formula, 2b in the category of the Internal Revenue Department, consists of 100 parts by volume of ethyl alcohol and  $\frac{1}{2}$  part benzol, and requires a permit for its purchase and a deposited bond to guarantee that it will not be used for beverage purposes.

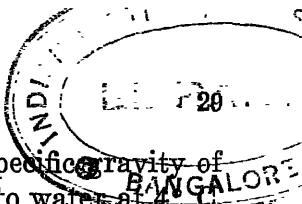
No. 1 denatured alcohol, containing only wood alcohol as a denaturant, obtainable without bond, is to-day probably the most widely used formula. A new denaturant became official in 1927, replacing pyridine. This is "aldehol," an oxidized

kerosene product, and its action on spirit-soluble gums and on lacquer is as yet unknown.

All ordinary alcohol contains about 5 per cent of water, for it is impossible by distillation alone to separate completely these two components. Alcohol free from water, called anhydrous or absolute alcohol, is now made in quantity by a continuous distillation process wherein alcohol with a small percentage of water is distilled with carbon tetrachloride or benzol, this ternary system permitting of the production of alcohol of 99 per cent purity. Another recent method for securing absolute alcohol, the Van Ruymbeke process, U. S. Patent 1,474,216, uses a tower filled with glycerine containing potassium carbonate to absorb the water from alcohol vapors passed through it, and the glycerine is constantly revivified by heating to 150° C. These processes are much more efficient than the previous one wherein the alcohol was distilled over lime, and afford an unlimited supply of absolute alcohol at a price only slightly higher than the commercial material. Recent researches have indicated that the use of anhydrous alcohol and esters makes a great improvement in pyroxylin solutions, both as regards solvent action and freedom from blushing. A substance known as Ansol has been placed on the market as a pyroxylin solvent at a low price, and consists of absolute alcohol with a small percentage of anhydrous ethyl acetate. It was claimed that this combination of low boiling solvents would not blush, as any condensed water would dissolve in the mixture and evaporate with it. It required a special pyroxylin for its use, however, and as far as known is still in the experimental stage. The development of a cheap, non-blushing solvent may come from this source, however, and will be a great boon to the industry.

Alcohol is a colorless liquid of familiar odor, with a boiling-point of 78.3° C. It mixes in all proportions with water, esters and the coal-tar hydrocarbons such as benzol and toluol. The petroleum hydrocarbons, such as gasoline, give a turbid solution with alcohol containing water, although they are per-

## SOLVENTS



fектly miscible with absolute alcohol. The specific gravity of absolute alcohol at 20° C. is 0.7893 referred to water at 15° C. The commercial product, containing alcohol, water and denaturants has a specific gravity of approximately 0.812 and weighs 6.75 pounds to a gallon. For further details, including methods of analysis, the reader is referred to Worden or to Allen's Handbook of Organic Analysis, Vol. I.

Alcohol by itself has no perceptible solvent action on pyroxylin. Special pyroxylins have been developed which seem to be quite soluble in alcohol. However, since other solvents must be used to avoid blushing, and for other reasons, there does not seem to be much advantage for this A. S. cotton over the usual variety, except for brushing lacquers, where a preponderance of alcoholic solvents is usually indicated. In conjunction with camphor, however, it gelatinizes the cotton and is thus of great importance in the celluloid industry. Ether, a product derived from alcohol by heating with sulphuric acid to 140° C., is also a non-solvent for pyroxylin, but it was early found that a mixture of the two, preferably in the ratio of 3 parts ether to 1 part alcohol, was an active solvent and the first pyroxylin solutions, the collodions, were made with this mixed solvent. These are still used in pharmacy, although the tendency is to substitute ethyl acetate. The reason for the solvent action of a mixture of non-solvents has not been settled, but it is a frequent observation among men working with colloidal solutions of rubber, gums, etc., that mixtures of solvents often given startling increases in solvent power. Alcohol is used in most lacquer formulae, partly for reasons mentioned above, partly because it seems to help the film flow out smoothly, and partly because of its excellent solvent power on many of the gums, resins and oils used in the formulae. Its greatest use, however, is in the production of ethyl acetate (q.v.).

The chief source of alcohol is the fermentation of molasses and in fact any cheap sugar or starch-containing material. The essentials of the process are in general familiar to the

public, many of whom have of late become proficient amateurs. A recent development that is already of importance in Europe and may ultimately prove so here is the synthesis of alcohol from acetylene, which is made by the action of water on calcium carbide, a product of the heating together of lime and coke in the electric furnace. This acetylene is transformed to acetaldehyde by the action of water containing sulfuric acid and mercury sulfate and the acetaldehyde changed to alcohol by the action of hydrogen gas in the presence of a nickel catalyst. In such a country as Switzerland, where grain is comparatively expensive and water power cheap, this process has already had some commercial success. Alcohol can also be produced from the ethylene found in coal gas and in the gases from petroleum cracking, by absorbing it in concentrated sulfuric acid, thus forming ethylsulfuric acid, and then hydrolyzing this with water to alcohol and sulfuric acid. This method has great possibilities, and in fact is already being used as a source of isopropyl alcohol, propylene being used instead of ethylene. Another possible future source of alcohol is wood pulp or sawdust, which can be transformed by acids to a fermentable sugar. At present the economic conditions in this country are unfavorable to this process, which has been rather thoroughly worked out both from plant and laboratory angles, but with the rise in price of molasses, corn and the alcohol derived therefrom, the point may soon be reached when ethyl alcohol from wood (not wood alcohol) may be advantageously produced. We may yet see a huge pyroxylin industry arise in the Pacific Northwest, the lumber center of the country, wherein waste wood will be converted to pyroxylin on the one hand and solvents on the other. The problem of securing cheap alcohol becomes more important when it is considered that the future of the motor fuel industry depends in large measure on the solution of this problem. Gasoline cannot last forever, neither can the coal from which benzol, the present substitute, is derived. Alcohol seems at present the inev-

itable motor fuel of the future, and to-day in Europe it has already achieved a prominent position.

### Fusel Oil.

During the rectification of alcohol, certain high boiling fractions are accumulated and form the fusel oil of commerce. Fusel oil is a mixture containing some alcohol and water, a little propyl, butyl, and isobutyl alcohol, and a high percentage of various amyl alcohols, especially the isobutyl carbinol  $(CH_3)_2\text{CH}:\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\text{OH}$ , and the secondary butyl carbinol,  $\text{C}_2\text{H}_5\cdot\text{CH}(\text{CH}_3)\cdot\text{CH}_2\text{OH}$ . Formerly disregarded, its use in spirit varnishes and as a source of amyl acetate for pyroxylin solutions led to a rapid increase in the price of fusel oil, which now sells for from 4 to 6 times the price of alcohol.

Crude fusel oil is a liquid of yellow to orange color (occasionally green) of an indescribable but characteristic odor that has a tendency to cause sneezing and coughing. It has been presumed to be poisonous, but recent medical tests have failed to show any toxic effect appreciably greater than that of alcohol itself. It contains variable percentages of the desirable high boiling alcohols, generally 70 to 80 per cent for a good grade crude fusel oil. The boiling point range is determined by distilling 200 cubic centimeters of the oil from a 300 c.c. distilling flask, collecting the distillate in a 200 c.c. graduated cylinder, and observing the volumes distilled over at 5° increments of temperature. A good product should give 60 to 80 per cent between 110 and 135° C., with practically no residue. The color of the distillate should be no more than a faint yellow. It should contain no free water.

The specific gravity of commercial fusel oil, as determined either by the pycnometer or Westphal balance should be from 0.81 to 0.835.

Inasmuch as revenue laws classify fusel oils containing more than 10 per cent of ethyl alcohol as dutiable under the latter heading, a standard test has been devised to determine

the percentage of lower alcohols and water in the crude fusel oil. A pear shaped flask with an elongated and graduated neck is used. The graduations run from 0 to 100. The bulb, which holds three times the volume of the neck, is filled to the lower mark with a saturated salt solution, fusel oil added to the upper mark and the flask carefully shaken and rotated. The lower alcohols and water dissolve in the salt solution and the dividing line between the two liquid layers moves up to a definite point on the graduated scale. From this the percentages of ethyl alcohol and water can be easily calculated.

While crude fusel oil is used directly in the production of technical amyl acetate, the high grade ester requires the use of a refined oil. The refining consists in a distillation and rectification through the well-known column stills. The product is free from water and ethyl alcohol, contains small amounts of propyl, butyl and isobutyl alcohols, but is in effect a mixture of amyl alcohols boiling from 120° to 135° C. Its density is 0.811, and it weighs 6.76 pounds to the gallon.

Like ethyl alcohol and butanol, fusel oil is used in lacquer formulae to smoothen the film, and it also seems to have a distinct value in preventing blushing to some extent, although it apparently has no direct solvent action on pyroxylin. Care should be taken to use it only in conjunction with amyl acetate or butyl propionate as with lower boiling solvents a point may be reached where the slower evaporating fusel oil will be in such excess as to throw out the pyroxylin. Fusel oil is an excellent solvent for gums, resins and oil and in high grade lacquer formulae it still has a definite place despite the lower price of its competitor, butanol. It is also used to a large extent in spirit varnishes, where its solvent power and high boiling point render it very useful.

Synthetic amyl alcohol is now an article of commerce under the name of pentasol. It is a mixture of various amyl alcohols of a high degree of purity, and both it and the acetate thereof are rapidly supplanting the fusel oil derivatives in the lacquer industry. Pentasol is made from casing-head

gasoline, or, rather, from the pentane fraction. The carefully distilled fraction is made to react with chlorine gas, giving a mixture of chlorpentanes with hydrogen chloride as a by-product, which is absorbed in water and sold. The purified chlorpentanes are next hydrolyzed to pentasol by the use of dilute caustic soda, separated, redistilled and fractionated. Pentasol consists of about 75 per cent normal amyl alcohols and 25 per cent of secondary alcohols, and despite the use of chlorine in manufacture, is free from the undesirable impurity when sold.

The pentasol plant in West Virginia is ideally located. Not only is the proper gasoline abundantly available there, but a neighboring alkali works is able to supply both chlorine and caustic soda. Fuel and cooling water are also abundant and cheap. It is quite possible that a rise in the price of corn, coupled with a reduction in the cost of producing pentasol, may make the latter a very serious competitor of butanol, over which it has the advantage of a higher boiling point and hence less tendency to blush.

### **Normal Butyl Alcohol, Butanol, C<sub>4</sub>H<sub>9</sub>OH.**

Till shortly before the World War, normal butyl alcohol was a rare chemical curiosity produced in small amounts at great expense through complicated syntheses. The perfection of the Weizmann fermentation process (U. S. Patent 1,315,585), has made it an article of commerce produced by the millions of pounds at a price considerably below that of fusel oil. Although its boiling point, 117° C., is lower than that of amyl alcohol, it is still high enough to serve most purposes, while the fact that it is produced as an almost chemically pure product gives it a great advantage over the fusel oil alcohols which contain a variable and at best limited percentage of high boiling constituents. Another advantage is the color, which is practically water white. The odor of butanol is much more agreeable than that of fusel oil, a point of im-

portance where material is sprayed and the factory permeated by the odor of the solvents. Like ethyl alcohol, butanol is a non-solvent, and its greatest use is in the production of butyl acetate. However, appreciable percentages, as high as 25 per cent, of butanol are incorporated into many lacquer formulae, as it has been found that this alcohol permits of a smoother and more lustrous film being deposited.

Butyl alcohol has a specific gravity of 0.81 and weighs 6.75 pounds to a gallon. The commercial product is practically free from water and boils almost entirely between 114° and 117° C. The flash point is 35° C.

The raw material for the production of butanol is corn, and for this reason the plants are located in Illinois and Indiana, in the heart of the corn belt. The corn is made into a 7 per cent mash, inoculated with a special bacterium (*B. granulobacter* or *B. amylobacter*) and fermented at 37° C. for 24 hours. The mash is rectified and in the distillate are found some water and ethyl alcohol, about 30 per cent of acetone and about 60 per cent of butanol. From 100 parts of corn, 5.36 parts acetone and 10.72 parts butanol are obtained. A small amount of a higher fraction, called "yellow oil" accumulates and this contains some of the higher alcohols, such as hexyl alcohol, together with other ill-defined compounds. In the fermentation considerable quantities of carbon dioxide and hydrogen gas are evolved, which are saturated with the acetone and butanol. These gases may be purified by the Bregeat system, whereby they are passed through scrubbing towers containing cresol, which dissolves the liquid constituents. The cresol is then heated and the vapors of acetone and butyl alcohol driven off, fractionated and condensed.

The rising price of corn has caused considerable research to be done on the possibility of utilizing cheaper raw material. In U. S. Patent, 1,510,526, Robinson claims the use of molasses as a source of butanol, and a process of purifying it so as to permit of fermentation by the *granulobacter* with satisfactory yield. He states that the preferable method is to combine

the molasses with corn, as the nitrogen found in the latter is necessary for the vigorous growth and action of the ferment. If this prove commercially successful, a reduction in cost of butanol may be expected.

The synthesis of butanol has been several times announced of late. The basis of these syntheses is acetaldehyde, prepared as described under ethyl alcohol, from acetylene and water. For the production of synthetic butanol, acetaldehyde is condensed to aldol by means of traces of alkali at a low temperature. This aldol, when neutralized and heated, yields crotonaldehyde, a most offensive substance. Crotonaldehyde, when treated with hydrogen over a nickel catalyst, yields butyl aldehyde and butanol. It is asserted on good authority that the present imported butanol is made in Germany by this process. The obstacles in the way of this synthesis are numerous. In the first place the making of the acetaldehyde is somewhat dangerous and expensive. The condensation to aldol is easy and complete, but the production of the crotonaldehyde is attended with considerable loss due to resinification. Further resinification occurs in the hydrogenation of crotonaldehyde, and a still further reduction in the yield occurs due to the formation of dibutylene glycol and similar products. Moreover, it is difficult to remove the crotonaldehyde completely from the synthetic butanol and only a trace makes the odor of the material unpleasant. The residual crotonaldehyde darkens in the light, due to resin formation, and thus affords another disadvantage. None the less, any sharp increase of price of butanol will undoubtedly tend to bring the synthetic material to the front, as the large carbide and acetylene producers have been researching intensively into this field.

### Cyclohexanol.

This alcohol, and the acetate thereof, have been produced in quantity abroad, especially in Germany, under the name of "hexalin," and one American firm has commenced to pro-

duce them. It is made by the hydrogenation of phenol, or carbolic acid, in the presence of nickel and under high pressure. It differs from the alcohols previously considered in having a ring structure instead of an open chain formation, and in being a secondary instead of a primary alcohol. It resembles amyl alcohol closely in its physical properties, and the cyclohexyl acetate made from it resembles amyl acetate to a striking degree. The acetate is an excellent solvent for pyroxylin, and owing to its high boiling point, 170° C., is of considerable value as a retarder or fortifier to prevent blushing. The price is high, owing to the high price of the raw material. It must be remembered, however, that phenol has been sold in recent years for a price of about ten cents a pound, and if it should again reach that level would be a prospective source of cyclohexanol for this purpose. A difficulty to overcome would be the tendency of cyclohexanol to lose water and become cyclohexene when treated with sulfuric acid and acetate of lime in the process of esterification, as this causes a substantial decrease in yield of the cyclohexyl acetate desired. By using glacial acetic acid with a little sulfuric acid as catalyst this decomposition can be minimized.

### ESTERS

Esters, or compounds resulting from the reaction between alcohols and acid have been made in many ways, but only two or three have any importance for the pyroxylin industry. The principal method consists of adding concentrated sulfuric acid to the cooled alcohol, mixing thoroughly, and then adding the solution to acetate of lime in a copper reaction kettle. The acetate of lime is a somewhat impure product containing a little water, calcium carbonate, and small amounts of calcium formate, propionate and butyrate. It averages about 83 per cent calcium acetate.

Many makers of esters to-day are using the glacial acetic

acid or even the 85 per cent acid directly instead of the acetate of lime and sulfuric acid method. Concentrated acetic acid is now obtainable at a reasonable price, and an additional advantage to this method is the absence of the residual sludge of calcium sulfate, the disposal of which has been a matter of serious concern to many ester manufacturers. For esters other than acetates, such as propionates, lactates, etc., acetic acid is replaced by the proper acids and the reaction carried out as before. Small amounts of concentrated sulfuric acid are used to catalyze this reaction.

The reaction takes place with the evolution of heat, and when complete ethyl acetate is distilled off directly, while butyl and amyl acetates are steam distilled. In either case the first product is rectified by fractional distillation, the water layer obtained in the first distillation being treated separately to recover the dissolved ester. Although amyl and butyl acetates boil at a temperature higher than water and can thus be easily freed therefrom, ethyl acetate affords greater difficulty. The commercial product is liable to contain water and ethyl alcohol, as well as small amounts of aldehyde. The final step in the preparation of ethyl acetate commercially is a drying over calcium chloride, which fixes most of the water and some of the alcohol. The high boiling esters are simply distilled until two layers, one containing water saturated with ester and one ester saturated with water, appear. The lower layer is removed, to be treated later and the distillation continued. The boiling points between which the ester is collected depend on the specifications of the purchaser or the maker.

### Ethyl Acetate.

Ethyl acetate is one of the most important of all the pyroxylin solvents and the amount used annually probably exceeds that of any other. It is a pleasant smelling liquid, boiling at 77° C. when pure, although the commercial product may boil anywhere between 70° and 80°. Its density, 0.883, is

rather high, so that a gallon weighs 7.39 pounds. The commercial product generally contains about 85 to 90 per cent of the ester, the rest being alcohol with a small amount of water. Some samples have been found to contain small amounts of ethyl propionate and butyrate, derived from the impure calcium acetate used, but such impurities are really an advantage to the solvent user.

The preparation from denatured alcohol and calcium acetate has been mentioned, but the largest single producer of ethyl acetate is reported to use a different method. The raw materials are alcohol and a weak vinegar made from it by air oxidation in the presence of certain molds. These are mixed, a small amount of sulfuric acid added, and the small percentage of ethyl acetate continuously separated by a complicated system of stills and columns described in detail in U. S. P. 1,454,462. While the initial cost of the equipment for this process is too high to make it economical for small producers, it seems to have been found successful on the scale at which the owners of the patent work. It is a remarkable variation from the accepted rule that yields of esters are improved by keeping the acid and alcohol concentrations at a maximum.

A third method of preparing ethyl acetate, used to some extent abroad but apparently not at present economical in this country, uses the ubiquitous acetaldehyde from acetylene so often mentioned. It has been found that under the influence of certain catalysts acetaldehyde condenses to ethyl acetate with high yields. The best catalyst is aluminum ethylate, made by heating aluminum turnings with absolute alcohol and a little iodine. In German Patent 308,043, the claim is made that by adding 3 to 5 per cent of aluminum ethylate to acetaldehyde dissolved in solvent naphtha a rapid formation of ethyl acetate with a yield of over 85 per cent is obtained. Such a product would probably contain some unchanged aldehyde, which would be undesirable in lacquers owing to its tendency to become yellow and deposit resin on standing.

**Tests.**

Esters for lacquer purposes should be tested for acidity, boiling range, ester content and water content. The acidity can be determined qualitatively by immersing a strip of clean copper in a test tube of the material and noting whether a perceptible green tinge is given to the metal. A more accurate determination is made by dissolving 5 c.c. in 20 c.c. of alcohol previously made neutral by the addition of a drop of phenolphthalein solution and decinormal sodium hydroxide till the pink tinge appears. Another drop of the indicator is added, and the titration continued till the color reappears. Each cubic centimeter of alkali corresponds to 0.006 gram of acetic acid, and no more than  $\frac{1}{2}$  to 1 c.c. should be required. For more accurate determinations N/100 alkali should be used.

The boiling-point range is determined by distilling 200 c.c. from a 300 c.c. balloon flask through a Hempel column filled with glass beads and fitted with a side arm, Liebig condenser and a thermometer. Heat should be applied slowly and regularly, and the distillate caught in a 200 c.c. graduated cylinder. Readings of the amount distilled over are taken at every 5° rise in temperature. Ethyl acetate should boil between 70 and 80° with about 60 per cent between 74 and 78°.

Actual ester content is generally determined by saponification; 4 to 6 grams of the ester are weighed accurately into 50 c.c. of a normal solution of sodium or, better, potassium hydroxide in alcohol. The flask is fitted with a long reflux condenser, a water bath is placed underneath and the solution boiled for one hour. It is quickly cooled and titrated with normal sulfuric acid, using phenolphthalein as indicator. Some chemists prefer to carry on the saponification in a 100 c.c. flask which is closed by a rubber stopper fastened down by wire. This is placed in a water bath and heated to 80 or 90° C. for three hours and then treated as above. In any event, a blank run should be made on the alcoholic alkali at the same time and the difference calculated back. Correction

should also be made for the free acid in the material. One cubic centimeter of normal alkali is equivalent to 0.088 gram of ethyl acetate.

A quick and simple method for determining the ethyl acetate content consists in adding the material to an equal volume of saturated calcium chloride in a graduated cylinder provided with a ground glass stopper, shaking thoroughly, and noting the diminution in volume of the upper layer. If 100 c.c. volumes are taken, and after shaking the upper layer is only 86 c.c., it can be assumed fairly accurately that 14 per cent is ethyl alcohol and water and 86 per cent ethyl acetate. Of course the presence of such substances as benzol would throw the results very far off, but in the ethyl acetate of commerce this could be present only by deliberate adulteration and scarcely to be considered. Where more than 20 per cent of alcohol is present the method is inaccurate, but practically none of the material met with comes under this heading. In fact a product containing 98 to 99 per cent of ester can be obtained for only a slightly higher price than the ordinary material.

The water content of esters is generally determined by noting how many volumes of gasoline can be mixed with one volume of ester without producing a turbidity. Two or three cubic centimeters of ester are placed in a 25 c.c. graduated cylinder with a ground glass stopper, and gasoline of 72° Baumé added gradually until a turbidity appears. Ethyl acetate should be miscible with at least 4 volumes of 72° gasoline.

### **Butyl Acetate.**

The ester is made by adding sulfuric acid slowly to the butanol and then running the hot butylsulfuric acid into a kettle containing a slight excess of calcium acetate. The mixture is kept at about 100° C. by steam coils and is mechanically agitated during the reaction. Steam is passed in and the mix-

ture of butyl acetate, butanol and water condensed. The oil layer is separated, rectified by distillation and the fraction between 110 and 125° collected. The watery layer is separately distilled and the ester and alcohol recovered.

This ester can also be made from concentrated acetic acid and butanol, using sulfuric acid as a catalyst.

Butyl acetate boils at 125° C., has a pleasant odor, is miscible with almost all organic solvents, has a density of 0.872 at 16° C. and while slightly inferior to ethyl acetate as a solvent for pyroxylin is far superior in its resistance to blushing. It may be remarked here that as far as actual solvent power is concerned ethyl acetate is superior to butyl, and butyl to amyl acetate. The tests for butyl acetate are practically the same as for ethyl acetate, and it is generally a higher grade product. The ester content averages 85 per cent, the residue being butanol. It is practically anhydrous and should be miscible with at least 20 volumes of gasoline. A typical distillation range as given by the makers is, below 107° C., 0; 107 to 120°, less than 40 per cent; 120 to 133°, 55 to 60 per cent; over 133°, less than 5 per cent.

### Amyl Acetate.

Besides being made by the method outlined for butyl acetate, amyl acetate may be made by passing a mixture of ethyl acetate and amyl alcohol with a little sulfuric acid through a heated rectifying column from which the high boiling amyl acetate is continuously drawn off (U. S. Patent 1,433,308). By this means it was found possible to use the cheap dilute acetic acid from alcohol oxidation by vinegar ferment, for this is converted to ethyl acetate as previously described and then utilized as above.

Amyl acetate comes on the market in various grades, containing different percentages of true amyl acetate. The technical grade contains a high percentage of lower acetates and

is not generally used by the lacquer trade. It has a use in other industries, such as in insecticides, where it is used as a bait for grasshoppers and cutworms. The better grade boils from 120 to 146° and is chiefly amyl acetate and amyl alcohol, while a still finer product, boiling from 135 to 140° is made for the pharmaceutical, perfume, and flavoring extract trades. The intermediate quality is the one chiefly used in lacquers.

The odor of amyl acetate is familiar to most people, and is aptly described by the name "banana oil" given to the product. It contains about 85 per cent of the ester, has a density of 0.860 to 0.866, is almost completely miscible with gasoline and as has been stated frequently is a very excellent solvent for pyroxylin. Despite the comparative cheapness of butyl acetate, amyl acetate is still used largely by the lacquer industry, primarily because of the rigorous specifications of certain large users of lacquers who do not care to experiment with the newer solvents, and partly because an amyl acetate solution will stand far worse conditions of humidity without blushing than even butyl acetate. It gives slightly more viscous solutions than the previously described solvents, which is at times an advantage and at other times a disadvantage. The tests for this ester are similar to those for butyl acetate.

A high-grade amyl acetate, called pent-acetate, is now on the market, being made from pentasol or synthetic amyl alcohol by the use of concentrated acetic acid and small amounts of sulfuric acid. The advent of this rigidly controlled material will be welcomed by users who have suffered in the past from variations in the quality of their amyl acetate, due partially to variability of fusel oil, and partially to greed and laxity on the part of some manufacturers.

### Butyl Propionate.

The appearance of this ester on the market in the last year is an interesting phenomenon. Propionic acid has been

made in small quantities by fermentation of whey (U. S. Patent 1,470,885) by means of the *Bacillus acidi propionici* in the presence of calcium carbonate. This process takes about ten days at a temperature of about 38° C., and is followed by liberation of propionic acid by sulfuric acid, distillation, and rectification. However, the acid produced by this process seems a little too expensive, and the butyl propionate of commerce comes from another source. During the war, the Hercules Powder Company produced a large amount of acetone by the fermentation of the kelp sea-weed of Southern California. The mixed organic acids thus obtained, neutralized by lime, supplied large quantities of calcium acetate which was fractionally crystallized and converted to acetone by heating. A residue called "taffy" accumulated, consisting chiefly of calcium propionate with small amounts of calcium acetate and butyrate. After the war the production of kelp products was stopped, but the huge accumulation of taffy was purchased by an Eastern concern and is now being converted to butyl propionate and butyrate for the lacquer trade.

The mixed calcium salts are dissolved in water, carefully separated by fractional crystallization and the calcium propionate treated with butylsulfuric acid as described under butyl acetate. The product contains about 5 per cent of butyl acetate and 5 per cent of butyl butyrate, the rest being butyl alcohol and butyl propionate. The boiling point range is between 125° and 160°, with the bulk of the material distilling over between 135 and 150° C. Pure butyl propionate boils at 150° C. The odor is quite pleasant, but for some purposes it has been found to linger too long. The producers claim that this is due to the small percentage of butyl butyrate, and are willing to supply a material free from this product. Unfortunately, this impurity is a potent factor in the good qualities of the solvent, as its high boiling point, 165° C., allows it to withstand almost any blush-inducing conditions.

As a solvent, butyl propionate is considered slightly in-

ferior to butyl acetate, and amyl acetates. It has the highest boiling point range of any ester solvent in commercial use and it is finding considerable sale, particularly in high grade products such as automobile enamels. Whether this commodity will be produced after the present supply of "taffy" is exhausted is uncertain, but the manufacturers claim the possession of a process for making propionic acid that will permit indefinite production of the ester if the demand continues.

### **Diethyl Phthalate.**

This commodity has achieved considerable prominence in the denatured alcohol industry and is now being produced in quantity. It is made from ethyl alcohol and phthalic anhydride. The catalytic process for making the latter substance has resulted in a marked lowering of the price. By this process the vapors of naphthalene, mixed with air, are passed over hot vanadium pentoxide, which catalyzes the oxidation to phthalic anhydride. By refluxing the anhydride with the alcohol diethyl phthalate is produced quite easily. It is a fairly good solvent for pyroxylin, has a high boiling point, and its use as a lacquer solvent is claimed in U. S. Patent 1,449,156, wherein it is combined with ethyl acetate and ethyl alcohol. In the author's experience it has been found that quantities sufficient to be of value linger too long in the film to permit of the average user employing it, except in small percentages as a plasticiser. It has a specific gravity of 1.129 and a boiling point of 295° C. It unfortunately does not seem compatible with many resins.

### **Diethyl Carbonate.**

This ester has just come forward as a pyroxylin solvent and little is known about its properties in this connection. It can be prepared from ethyl alcohol and phosgene gas, and since the latter material is easily made from carbon monoxide

and chlorine, all the raw materials are cheap and abundant. It boils at 126°, almost the same as butyl acetate and when pure has a pleasant odor. It is a poor solvent for gums and oils, and gives viscous solutions of pyroxylin which do not permit of much dilution with hydrocarbons. The addition of 10-20 per cent of butyl alcohol to its solutions has a very beneficial effect.

### Beta-chlorethyl Acetate.

By passing a mixture of ethylene gas and chlorine into acetic acid, beta-chlorethyl acetate is produced. Here also the raw materials are cheap and the solvent power and high boiling point of the product (145°) of interest. However, a difficulty in the use of almost all chlorinated esters such as the above, ethyl chloracetate, and chlorpropyl acetate, seems to be that they have a tendency to liberate free hydrochloric acid, which is of course a very serious disadvantage. The use of the beta-chlorethyl acetate is described in German Patent 362,747.

### Ethyl Lactate.

This solvent is steadily growing in favor, despite its comparatively high price. It is made by esterifying lactic acid with ethyl alcohol, both products being made by fermentation. For producing lactic acid starchy or sugary materials are converted to fermentable sugars by boiling with acids or by the action of malt diastase. Fifty per cent by weight of calcium carbonate, 5 per cent skim milk, and pure cultures of lactic acid bacilli are added and the fermentation carried on at 40 to 50° C. for 10 days. The lactic acid formed reacts with the calcium carbonate to give white crusts of calcium lactate from which lactic acid can be prepared by treatment with dilute sulfuric acid.

Ethyl lactate is a clear mobile liquid boiling at approximately 150° C. Its odor is slightly unpleasant but disappears

quickly. It is slightly heavier than water, weighing 8.65 pounds to the gallon.

The high boiling point and great solvent power of the ester make it an attractive ingredient in high grade formulae. To this may be added the fact that it can be diluted very considerably with petroleum or coal tar hydrocarbons—and it is claimed that even 25 per cent of water can be added to the material without precipitating the pyroxylin. Another point in its favor is that it is not easily ignited, having a flash-point of 115 to 120° F.

Ethyl lactate is generally used to the extent of 5 to 15 per cent of the total volume of the formula and undoubtedly has a beneficial effect on the resistance of the film to blushing and on the smoothness of the final coat. A lower price should mean a wider use for this interesting solvent.

One unfortunate feature of ethyl lactate seems to be its tendency to hydrolyze. There is an impression in the trade that the many cases of thickening on standing of brushing lacquer enamels are due to this hydrolysis and the reaction of the free lactic acid on the pigments.

Butyl lactate is now available and it is understood that it is more resistant to hydrolysis as well as having an even higher boiling point. The vapor-pressure curve of the lactates indicates that they rank at the head of solvents, in so far as slow evaporation is concerned, an ideal condition for brush and flow-coat lacquers.

### KETONES

Ketones, or products containing the formula grouping R.CO.R', where R and R' are organic radicals, have long been used as solvents. Indeed, the early reports that wood alcohol dissolved pyroxylin are due mostly to the fact that commercial wood alcohol or methanol contains small quantities of acetone, the simplest ketone. Acetone, methyl acetone, light and heavy acetone oil, diacetone alcohol and mesi-

tyl oxide are all of this class and all are used as solvents for pyroxylin. As a class they are as good or better solvents than the esters. Their odors, particularly those of the acetone oils, are much less pleasant, but since acetone oils are the cheapest high-boiling solvents at present available, many of the largest lacquer producers incorporate 2 to 10 per cent of these evil-smelling ingredients into their formulae. The odor is often partially masked by the use of safrol or oil of wintergreen, but it seems impossible to prevent its characteristic stench from lingering. Only economy born of stern competition can justify the use of acetone oils, and nothing can justify it when the lacquered article is to be worn or carried near the human nostril.

### Acetone.

The production of acetone as an accompaniment to the fermentation process of making butanol has already been mentioned. During the war it was made by two other fermentation processes, neither of which is at present being used. They were first, the fermentation of the giant kelp of the Pacific coast, followed by neutralization by lime of the mixed organic acids formed, separation of the calcium acetate, and formation of acetone therefrom by heating to 290° C. The second method consisted in fermenting molasses to ethyl alcohol followed by an oxidation by air under the influence of certain molds to vinegar, concentration of the vinegar to acetic acid, followed by passing the vapors of acetic acid over lime at 400 to 500° C. This is the Squibb method for making acetone, and depends upon the fact that lime and acetic acid at that temperature react to give calcium acetate which immediately breaks up into acetone and calcium carbonate, the latter being capable of reacting with further acetic acid.

Another method of making acetone from alcohol was also utilized during the war by an English firm. They passed alcohol vapors over hot copper, thus securing acetaldehyde

and hydrogen. The latter was utilized to make hard fats of the Crisco type from vegetable oils. The acetaldehyde was oxidized by air to acetic acid, and the latter treated as above. This process has also been abandoned, as has a similar one starting with acetaldehyde made from acetylene as previously described. The acetone of commerce is made either by the butyl alcohol fermentation or by the distillation of hardwoods.

Wood distillation is an old art, its original purpose being the production of charcoal. Hard woods, such as birch, beech, oak, etc., are used. After being cut into billets they are placed in steel cars which are wheeled into a retort which is heated to 160 to 280° C. The volatile matters distill off and are collected as two layers, one of tarry matter and one an aqueous distillate containing almost as many ingredients as coal tar. The important constituents of this crude pyroligneous acid, as it is called, are acetic acid, wood alcohol, acetone and methyl acetate, with appreciable quantities of higher ketones. In the tar are found the valuable creosote and the creosote phenols which are extensively used in medicine. Charcoal is left as a residue in the retort.

The watery layer is separated from the tar and distilled after being neutralized with lime. Crude wood naphtha, containing wood alcohol acetone, and methyl acetate distill over and the residue, on evaporation gives the gray acetate of lime of commerce, an impure calcium acetate containing some tar, salts of other fatty acids and averaging 80 to 85 per cent calcium acetate. This is used in great quantities in the preparation of the acetic acid esters of various alcohols, as described previously. Gray acetate of lime, heated under mechanical stirring to about 290° C. yields acetone and acetone oils which are separated by fractional distillation.

The acetone produced in the original distillation is generally recovered as methyl acetone, a mixture containing about 50 per cent wood alcohol, 25 per cent acetone and 25 per cent methyl acetate. This mixture is used in paint and varnish removers, and as a solvent for gums and is found in many of

the lacquers now on the market. Both methyl acetate and acetone are good pyroxylin solvents and the wood alcohol is a good ingredient in itself, due to its solvent action on gums.

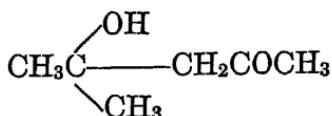
Acetone is a colorless liquid with a characteristic slightly unpleasant odor. It boils at 56° C. and has a specific gravity of 0.792 at 20° C., weighing 6.6 pounds to the gallon. It is probably as good a pyroxylin solvent as any in common use, that is, solutions in acetone have a lower viscosity for definite concentration than in any other popular solvent. Its great drawback is its low boiling point, which causes a marked blushing even under mild conditions of humidity. For this reason, it is never used alone as a lacquer solvent, except in special solutions used to remove lacquer from finished objects. A solution containing equal parts of acetone and benzine is excellent for this purpose and is quite cheap. Most of the patented varnish removers are of this type, with the addition of some wax or other dissolved substance to slow down the speed of evaporation and thus secure longer contact with the surface to be cleaned. The various inks used for writing on celluloid or lacquer films generally contain acetone which permits the ink to penetrate the film and which at the same time is miscible with water and acts as a solvent for the dyes used to color the ink.

### Acetone Oils.

In the distillate obtained from calcium acetate on heating as described above, are found not only acetone, but an appreciable percentage of a mixture of higher ketones and aldehydes. After removal of the acetone, the residue is fractionated and the fraction from 140 to 160° C. collected as "light acetone oil" and that from 160 to 220° as "heavy acetone oil." Both are used as varnish removers and as solvents, as previously mentioned. A method of partially deodorizing these oils is in use, but not wholly successful. Similarly, a project to hydrogenate them to mixtures of secondary alco-

holes from which esters could be made has failed to meet commercial requirements.

### Diacetone Alcohol.



This solvent is made by the condensation of two molecules of acetone under the influence of alkalis such as lime and baryta. An interesting chemical problem is involved, in that the equilibrium between acetone and diacetone alcohol in the presence of alkali lies heavily on the side of the acetone. To secure good yields it is necessary to remove the diacetone alcohol as fast as it is formed, and this is done by heating acetone in a kettle, condensing the vapors, and allowing them to flow through a layer of alkali on a porous support, preferably in an apparatus of the Soxhlet fat-extraction type. The mixture of acetone and diacetone alcohol flows back into the kettle, which is kept at about 80° C. higher than the boiling point of acetone and lower than that of the diacetone alcohol. By continuing this process the acetone is finally almost completely transformed to the diacetone alcohol, from which, in the absence of acid or alkali, it can be completely distilled.

Another method of preparing diacetone alcohol which is widely used consists in flowing acetone by gravity through iron drums containing lime. The equilibrium mixture thus formed flows into a steamjacketed still where the unconverted acetone is distilled off and condensed to be used over again, while the diacetone alcohol is tapped off.

U. S. Patents 1,075,284 and 1,082,424 and Lovell's article "Chemical Technology in the Shoe Industry," Chem. and Met., Eng., 28,715, 1923, deal with this interesting solvent.

Diacetone alcohol, which contains both the ketone and the alcohol groups is a colorless liquid, of very slight odor, boiling at 160°. It is an excellent pyroxylin solvent, almost im-

mune from blushing, and at the present prices of acetone can be produced quite cheaply. Its disadvantages are its extraordinary sensitiveness, as traces of alkali reconvert it to acetone, and its incompatibility with mixtures of pyroxylin and vegetable oils. Its use so far as is known is limited to a few concerns who employ it chiefly as a solvent for pyroxylin in the leather industry. Its specific gravity is 0.91 to 0.93, that of higher gravity containing more diacetone alcohol and less acetone.

### Mesityl Oxide.

If diacetone alcohol be heated with a little iodine or sulfuric acid, a molecule of water is split off and mesityl oxide is formed. This compound is also a ketone, possesses good solvent powers and boils at 132°, which is as high as amyl acetate averages and higher than butyl acetate. Its use has been patented recently, and it may eventually be an important solvent. Mesityl oxide adds hydrogen easily in the presence of finely divided nickel and becomes methyl-isobutyl ketone, a liquid of powerful camphor-like odor which boils at about 116° C. and is a good pyroxylin solvent. Its advantage over mesityl oxide are that it seems to be a somewhat more potent solvent, and is free from the tendency of the latter compound to become colored in the light. At present the interest in methyl-isobutyl ketone is merely academic.

### Camphor.

While not strictly a solvent, camphor is a ketone whose close connection with the pyroxylin industry merits consideration here. It is derived from a species of laurel tree grown chiefly in Formosa and its production is a monopoly of the Japanese government. Camphor dissolved in alcohol was one of the first-known pyroxylin solvents, and the celluloid industry depends on the fact that camphor and pyroxylin

form a solid solution with each other that is flexible, hard and moldable. At present camphor is occasionally found in lacquers, almost always being present when scrap celluloid or motion picture film has been used to prepare the solution. Sometimes, however, it is added deliberately for some fancied advantage of plasticity or gloss. In the author's opinion camphor is not only more expensive, but less suited as a pyroxylin latent solvent or plasticiser than its present substitutes, triphenyl and tricresyl phosphates, butyl tartrate or dibutyl phthalate, at least in so far as lacquers and enamels are concerned. It seems that in celluloid manufacture no really satisfactory substitute has been found. The gloss given by camphor soon fades, owing to sublimation of the camphor, and the surface of the film becomes somewhat rough and pitted. The odor, moreover, is persistent and unpleasant on articles used on or about the person.

Camphor is a familiar substance and needs little description. It is a white, translucent solid of a density of 0.992, a melting point of 176.4° C., and a boiling point of 205.3° C. It is slightly soluble in water and highly so in alcohol and acetone. It has a high vapor tension at ordinary temperatures, and thus sublimes away rapidly in the open air.

Against the natural camphor, which is subject to price manipulation by Japan, Germany holds a synthetic product prepared from turpentine that can compete under abnormal price conditions, although ordinarily its cost of preparation is too high for commercial production.

### **Aldehydes.**

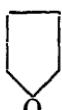
The only aldehyde of importance as a pyroxylin solvent is furfural. This substance has a most interesting history, having leaped from a very costly and rare chemical reagent to one of the cheapest organic chemicals in the space of a few years. It is now made on a large scale from corn cobs, by digesting with steam under pressure and then rectifying the

resulting water solution of furfural, and more particularly from oat hulls, the waste material from the preparation of oatmeal and a commodity produced in enormous quantity annually, by digesting with a dilute sulfuric acid solution in a steam heated rotary digester. The furfural is produced by the decomposition of pentosans which are the essential constituents of bran-like materials. Its price has dropped from \$20 a pound to 23c, and will go lower if a large scale demand is created.

Furfural, when absolutely pure and freshly vacuum distilled, is an almost colorless liquid, but it rapidly darkens in the light, and more slowly in the dark, to a yellow, red and finally almost black material. Moureu and Dufraisse have found that traces of certain substances inhibit this reaction, and the author has verified this in the case of hydroquinone especially. Furfural has a specific gravity of 1.159, is slightly soluble in water and boils under atmospheric pressure at 161°. It is best distilled under a reduced pressure, at a temperature below 120° if possible, and under these conditions the product remains colorless perceptibly longer.

Furfural is an excellent solvent for pyroxylin, and its high boiling point renders it well adapted as an anti-blush ingredient. It is cheaper than amyl acetate and boils at a considerably higher temperature. On the other hand its odor is extremely powerful and repulsive to most users, it yellows the film, and it is a poor solvent for most gums and oils, although claims, unsupported by proof, have been made to the contrary. Its use as an ingredient in paint, varnish and lacquer removers has recently been patented, and it can be well recommended for that purpose.

Work has recently been done by Adams and Kauffman (*J. Am. Chem. Soc.*, 45, 3029, 1923) on the possibility of hydrogenating furfural to amyl alcohol. While a certain amount was produced by this method, the yield was too small and the expense too great to warrant any further work in this field. More recently, furfural has been changed to fur-

furyl alcohol,  CHOH, on the one hand, and pyromucic or furoic acid on the other by the well-known Cannizarro reaction, whereby an aldehyde is heated with an alkali and yields equimolecular quantities of alcohol and acid. Esters of furfuryl alcohol, and ethyl, butyl and amyl furoates are now on the market and may prove to have some value as lacquer solvents.

Furfural, when condensed with phenol, gives resins analogous to Bakelite, and its chief present use seems to be in this field. Other resins, made by condensation with aniline and other amines, possess a yellow to black color and have been suggested for use in lacquers. They are sparingly soluble in most lacquer solvents, but quite soluble in furfural from which they are deposited as a highly colored lustrous film.

The cheapness and abundance of furfural, together with its great chemical reactivity and the consequent number of compounds that can easily be made from it render it a logical source of useful chemicals for industry in general and it may be expected that further research will adapt it or some of its products to the requirements of the pyroxylin lacquer manufacturers.

Among the furfural derivatives experimented with besides those mentioned above are tetrahydrofurfuryl alcohol, furfuryl alcohol and furfuryl acetate. An excellent article on these solvents is that by Trickey, Jour. Ind. and Eng. Chemistry, Vol. 19, 5, p. 643.

### Glycol Ethers.

One of the most interesting developments in the field of lacquer solvents has been the recent arrival on the market of the glycol ethers. As mentioned before, the solvent action of a mixture of alcohol and ether was early discovered and utilized in collodion manufacture. It was natural for chem-

ists to wonder if a compound that was at once an alcohol and an ether would not be a good solvent, and when the production of ethylene glycol and propylene glycol became a large-scale, inexpensive industrial fact instead of a laboratory experiment, it took little time for keen interest to be aroused in their derivatives, notably the various ethers thereof. Glycols are double alcohols, permitting of both mono- and diethers to be made from them, and while a large number of such compounds have been prepared, most of the interest and by far the bulk of the production has been devoted to the monoethyl ether of ethylene glycol, called CelloSolve for short, and to a lesser degree to the monobutyl ether of the same glycol.

CelloSolve is an excellent solvent for nearly all grades of nitrated cotton, being superior to butyl acetate in many ways. Its boiling point lies between those of butyl acetate and amyl acetate, being 134.8 C., but its speed of evaporation is considerably less than the difference in boiling point would indicate. This slow evaporation combined with high solvent power make it a very admirable solvent for brushing and flowing lacquers.

CelloSolve is remarkable among lacquer solvents in being practically odorless, a matter of great importance in many fields, particularly in household brushing lacquers, where many housewives had objected because of the odor of butyl and amyl lactates, and in lacquering the insides of refrigerators. Ordinary lacquers maintained a residual odor in closed containers for a very considerable period, imparting it to the food in many cases. Those using CelloSolve, alcohol and toluol diminished this tendency most considerably.

An interesting property of CelloSolve as a pyroxylin solvent is its ability to stand dilution with toluence and gasoline. It is superior even to ethyl lactate in this respect and much superior to butyl acetate, withstanding 1½ times as much gasoline and 2¼ times as much toluol before precipitation of the cotton as the latter solvent.

A difficulty with CelloSolve is its incompatibility with the usual lacquer resins, notably ester gum and dammar, in the presence of pyroxylin. Dammar can be made compatible and to give clear films if first dissolved in toluol and then treated with CelloSolve to precipitate the wax, a procedure quite similar to the usual dewaxing process of dammar by alcohol as outlined under "Dammar" in this volume. If mixed with properly treated dammar to no less than one-quarter of its weight, ester gum can also be utilized. There is no question in the author's mind, however, that combinations of CelloSolve with the usual solvents can be made that will permit of using ordinary dewaxed dammar and ester gum in any reasonable proportions without giving cloudy films.

The price of CelloSolve is approximately that of butyl propionate, and considerably higher than that of butyl acetate or amyl acetate. Judicious blending of this solvent with others seems necessary to maintain desirable qualities and yet meet competitive prices. The density of the material is higher than that of most solvents, as it weighs 7.8 pounds per gallon.

The acetate of CelloSolve has now appeared on the market and is finding wide use in thinners for automobile lacquers. This material has a very slight odor, weighs 8.1 pounds per gallon, and has a boiling point of 154° C.

A very complete account of the glycol ethers can be found in the article by Davidson, *Industrial and Engineering Chemistry*, Vol. 17, page 669, 1926.

### Miscellaneous Solvents.

The number of solvents proposed for dissolving pyroxylin is very great. A glance through the list painstakingly compiled in Worden's treatise shows how the whole field of organic compounds has been combed for likely solvents, and how patent protection has been claimed for myriads of rare substances. Rarity and present cost are no insurmountable

obstacles to the success of a good solvent, as the present use of butyl acetate, butyl propionate and furfural indicates. Ten or fifteen years ago these substances were as ridiculously impractical for the purpose as many whose mention now sets the lacquer maker into fits of laughter. But many of the solvents claimed in patent specifications would be of little use at any price. The ideal lacquer solvent, besides minimum cost, should have certain definite properties. It should naturally be a good solvent for pyroxylin, gums and oils, miscible in all proportions with other solvents and non-solvents, have a boiling point between 135° and 160° C. and be lighter than water. It should preferably be odorless, or in any event of a pleasant odor, non-hygroscopic and non-toxic. It should be free from acid or alkali, and should not deteriorate on keeping. Such a solvent if procurable at a price of \$1 to \$1.50 a gallon would probably revolutionize the industry, and it would be a bold chemist who would deny that it may be produced at any time.

Some solvents, not hitherto described, merit brief mention. These include nitrobenzene, produced by the action of nitric and sulfuric acids on coal-tar benzol. This compound is a yellow liquid, boiling at 210° C. and smelling like bitter almonds. It readily dissolves pyroxylin and was one of the earliest used high-boilers. It dries too slowly, however; it is quite poisonous, and its present use is restricted to very small amounts sometimes added to disguise other smells. Safrol, a product obtained from oil of camphor and the odorous constituent of sassafras oil, is used for similar purposes, especially in leather dopes where it helps to counteract the unpleasant odor of the oils and the leather itself. Methyl salicylate, or oil of wintergreen, also belongs to this category.

Much space has been devoted in this volume to the solvents of pyroxylin, for not only is the proper choice of these solvents of great importance in the preparation of satisfactory lacquers, but the cost of making and consequently of applying these materials hinges chiefly upon this point. Varnishes

of the oil and resin type dry primarily by oxidation of the oil by the air under the accelerating action of the "driers" incorporated into the product. Only small amounts of turpentine or benzine are used as thinners and as result most of the applied material remains as actual covering film. Lacquers on the other hand dry by simple evaporation of the solvents and it can be readily seen that if we have, say one pound of solid material in a gallon of lacquer weighing about 7.5 pounds to a gallon, more than 80 per cent of the material applied goes off into the air. It is true that some large users, particularly in the film industry, recover their solvents, but this is impractical for the huge majority of lacquer users. As result every effort must be made to reduce the cost of this large percentage of wasted material, both by the use of cheaper solvents and by careful adjustment of the solvents and the much cheaper non-solvents so as to secure the desired effect at minimum cost. Such formulae as are often found in reference books, wherein 50 per cent or more of amyl acetate and amyl alcohol are used with the naive statement that a satisfactory product can thus be obtained, are absolutely impractical for present commercial practice. Of course the product is satisfactory, but no one will pay the price required.

## CHAPTER IV

### NON-SOLVENTS

With the increase in competition in lacquer manufacture it soon became necessary to discover methods of cheapening the product, and since the most expensive portion was the solvent, the most obvious step was to add to the solution a cheap non-solvent material as a substitute for as much of the expensive solvent as possible. Water is the cheapest non-solvent, but since it is immiscible with other ingredients and precipitates the pyroxylin, is absolutely unutilizable. The next cheapest materials are the petroleum and coal-tar hydrocarbons, such as benzine, benzol, toluol and solvent naphtha, and these are used in large quantities, more than half of many lacquer formulae being composed of these substances. The reduction in cost is very great, for amyl acetate at about \$2 a gallon or butyl acetate at \$1.50 is replaced by benzol or toluol at 25 to 40c. a gallon, and to some extent by petroleum benzine at 15 to 20c. Moreover, many of the resins are more soluble in the non-solvents than they are in the esters and the use of the hydrocarbons is thus an advantage.

The petroleum benzine is used in diminishing quantities, for the small amounts of water in the solvents are sufficient to cause a turbidity or even a separation into two layers when much of the benzine is used. The coal tar hydrocarbons, on the other hand, are miscible to the limit of pyroxylin precipitation without turbidity and they are used almost exclusively. It is true that fusel oil or butanol will serve to blend the esters and benzine, but their use involves an added cost that nullifies the initially lower price of the petroleum product.

The addition of benzol or toluol to a solution of pyroxylin in an ester should be done with thorough stirring, for otherwise a local precipitation of the pyroxylin will ensue and some trouble redissolving will be experienced. There is a gradual increase in viscosity reaching a maximum at the point just before precipitation. If this point is exceeded, there will be a sharp drop in the viscosity, for the pyroxylin will be in the condition of gelatinized lumps and the liquid will have only the very low viscosity of the organic solvents themselves.

The percentage of non-solvent that can be added depends on the accompanying solvent. With ethyl acetate or acetone solutions can be made with only about 20 per cent of the solvent, or even less for dilute pyroxylin solutions. With butyl or amyl acetate 30 to 35 per cent is generally used. A very important point to consider is that the rates of evaporation of the chosen solvents and non-solvents should be approximately the same, for otherwise a point may be reached in the drying of the film when the concentration of non-solvent becomes so great as to precipitate the pyroxylin in a non-coherent useless form. Consequently low boiling solvents are adjusted with benzol, and the higher boiling with toluol or solvent naphtha. If a low boiling non-solvent be used with a high boiling solvent there is danger of pinholing of a thick film. This effect is due to rapidly evaporating benzol bubbling through a layer of viscous solution and thus leaving tiny bubble marks or pinholes in the film. It is also conducive to the formation of wrinkly or pebbly films. Probably the best films are deposited from a solution containing only high boiling solvents but since these are impractical for most purposes the next best thing is to adjust the solvents and non-solvents so as to secure the effect of a uniformly evaporating single liquid. For example, a solution containing acetone and benzol, and butyl propionate and solvent naphtha would be fairly efficient insofar as resistance to permanent blushing and precipitation are concerned, but the wide gap between the boiling points of the

two sets of liquids is such as to leave a distorted film unless some such substance as fusel oil or butanol is present to smooth out the rate of evaporation and consequently the film.

In this connection it may be mentioned that the alcohols described in Chapter III, while non-solvents, are used not so much to cheapen the product as to impart definite qualities of lower viscosity, smooth flow and regular evaporation. Wood alcohol is also used as a non-solvent for pyroxylin lacquers, but has a definite place owing to its solvent power on gums, especially shellac.

### COAL TAR HYDROCARBONS

#### Benzol.

Benzol, toluol, xylol, and solvent naphtha are all obtained as by-products from the coking of coal, either for gas or for coke as a primary product.

The coal tar obtained by the destructive distillation of soft coal contains quite a high percentage of benzol and toluol, which are recovered by fractionally distilling the tar and collecting fractions from 78 to 85°, 85 to 115°, etc. Benzol occurs in the first fraction which also contains some thiophene, carbon disulfide and toluol. The thiophene is removed by treatment with sulfuric acid, and the carbon disulfide by careful fractionation. Benzol is sold in various grades, that for the aniline dye industry being a much purer product than the 90 per cent variety which is used by the lacquer trade. The latter contains nearly 10 per cent of toluol and some xylol. Most specifications call for a product that boils completely below 120°, with 90 per cent below 100° C. Twenty per cent should distill over at 85°.

Pure benzol, generally made by distilling benzoic acid with lime, boils at 80.36°, and freezes at 5.4° C. The commercial article contains enough toluol to depress the freezing point below any temperature liable to be encountered in storage, although cases have been known where benzol in outdoor

tanks has frozen. The density of the commercial article ranges between 0.86 and 0.885. It is sold in 50 or 100 gallon drums, and in tank car loads. The largest producers have warehousing and delivery facilities in large cities whereby daily tank-wagon deliveries can be made.

Benzol has been called one of the most poisonous industrial substances, but while it is true that many cases of benzol poisoning have occurred in the coal-tar industries any claims that it is a menace to the health of the sprayer or others in the factory where reasonable ventilation is used are disproved by the universal use of the product in lacquer formulae which have caused no recorded trouble. Much of the agitation against benzol is due to propaganda of the painters' unions against spray painting or lacquering. A bill has been pending in the New York legislature which would prohibit the use of any spraying device with a liquid containing any toxic ingredient. Such a bill would seriously hamper production in many factories, raise the cost of many articles, and is uncalled for by any appreciable harm caused by the use of any ingredient commonly met with in pyroxylin lacquers. It is true that some of the solvents used for cellulose acetate, notably tetrachlorethane, are very poisonous and should be prohibited, but that is another story.

Besides being tested for boiling point range, it is good lacquer practice to submit benzol and toluol to certain other tests. Acidity is determined by the copper strip test, and is sometimes present due to residual traces of sulfuric acid. The so-called wash test for impurities is made by adding 21 c.c. of the liquid to 7 c.c. of 98 per cent sulfuric acid in a flat-walled glass bottle, shaking, cooling and comparing the color with a series of standards made from water solutions of cobalt chloride, ferric chloride and potassium dichromate, and kept in similar bottles.\*

It sometimes occurs that benzol or toluol that passes the

\*N. B.—Complete specifications and tests of coal-tar hydrocarbons can be obtained from the Barret Company, 17 Battery Place, N. Y. Coke Oven Light Oil Distillates, 1922.

usual tests gives a markedly unpleasant odor when sprayed and the author has devised a test for this purpose that has so far given satisfaction. Five cubic centimeters of the hydrocarbon are added to 20 c.c. of N/20 potassium permanganate solution, shaken for 3 minutes, and then back-titrated with a standard N/20 ferrous ammonium sulphate solution containing 98 grams of concentrated sulfuric acid to the liter. If less than 3 c.c. of the permanganate solution have been consumed by the hydrocarbon the material was found satisfactory; if 3 to 4 c.c. it was dubious, while a consumption greater than 4 c.c. generally agreed with a nasal test of the odor and meant rejection of the material. It is difficult to agree on odors, and it was found that this test gave uniform results and prevented the complaints of consumers about the odor of the product. The odor is probably due to some ethylenic compounds which do not give the wash test.

Another test that it is well to make is to evaporate a few drops on a piece of white paper and note any colored or oily residue. Such dissolved matters are occasionally met with and are detrimental to the lacquer. (See the article by Weiss, "Commercial Benzol," J. Ind. Eng. Chem. 3, 10; 1911.)

### Toluol.

N. C. Commercial toluol, when distilled, should give the first drop of distillate at 110° C. and 100 per cent should distill over at 112° C. Pure toluol boils at 111° C. and has a density of 0.866. It freezes at a very low temperature. The tests for toluol are practically identical with those for benzol.

### Solvent Naphtha—Special Washed.

This term has been applied to a hydrocarbon mixture of rather wide distillation range, consisting chiefly of xylenes and cumenes. Nowadays there is a certain market for xylol as such, and as result the solvent naphtha is now mostly a mixture of various cumenes. The distillation range varies, from

8 to 30 per cent, boiling below 140° C. and 90 per cent below 160° C. The tests are about the same as for benzol and toluol. An average specific gravity for commercial solvent naphtha is 0.875. The odor is more unpleasant than either of its lower homologs, the possibility of undesirable residue is greater, and its high boiling point makes it unwise to use solvent naphtha in any great percentage. It is still used, however, by some manufacturers, although its advantages over toluol, despite a trifling price differential, are problematical.

#### **Benzine—V. M. and P. Naphtha.**

A deodorized petroleum product, called V. M. and P. naphtha (varnish-makers and painters) is used to some extent as its cost is a little below benzol or toluol. It is practically a gasoline of 100° to 160° C. boiling range although there may be considerable variation from these points. It has a low specific gravity, about 0.730, and as has been said before is not miscible with solvents containing a little water. Ordinary gasoline has also been used to replace benzol to some extent, when its price was low enough to produce an economy. The naphtha should pass the same tests as benzol and toluol.

## CHAPTER V

### **PLASTICISERS**

When collodion first was applied to cuts and scratches as a protective sheath it was noted that the film contracted and puckered on drying. For some types of cuts this was an advantage as the contraction drew the edges of the wound together and thus exerted a styptic effect. For most purposes, however, this property was undesirable in view of the pain caused by the contraction and the tendency to peel away from the skin. To overcome this the collodion was plasticized by camphor, Canada balsam and castor oil, and the flexible collodion of the Pharmacopoeia resulted.

When pyroxylin solutions began to be used for other purposes the same problem was encountered. The film bridged away from the metal, or was too brittle for use on supple material like leather or could not stand up under the warping of woods to which it was applied. Plasticisers were essential and the literature of the pyroxylin industry is cumbered with literally hundreds of compounds that are considered to be useful for the purpose. Of these only half a dozen or so are of any present practical importance.

The early celluloid or Zapon lacquers naturally used the camphor present in the celluloid as the plasticiser. This was fairly effective, but in time the camphor disappeared and the film became brittle. Moreover camphor is expensive, and a tremendous amount of research was carried on to displace it in celluloid manufacture. These were only partially successful as far as celluloid was concerned but the discovery of

triphenyl and tricresyl phosphates was a very valuable by-product and a boon to the lacquer industry.

The plasticisers are almost without exception esters or ketones, in other words solvents of high boiling point. It seems certain that a plastic film is really only a very concentrated solution, and that as soon as all the solvent has disappeared the original brittleness of the pyroxylin film asserts itself. The first plasticiser to replace camphor was castor oil. This was chosen because it was cheap, practically permanent in the film, light in color, slow-drying and thus not subject to the progressive hardening of linseed and similar oils. Even to-day it is used in great quantities, particularly in leather dopes and airplane dopes. But it has disadvantages, such as the development of a rancid odor on standing, and an unpleasant habit of making the film too soft if used in very slight excess. For the better grade lacquers and enamels tricresyl phosphate and dibutyl phthalate hold the stage at present, despite the fact they cost nearly three times as much as castor oil. The field is still open, however, for a plasticiser of reasonably low cost, very low volatility and high plasticising power in small percentages, particularly if it is odorless, colorless and permanent. Such a paragon would be received with open arms by the trade.

### Castor Oil.

Castor oil is derived from the castor bean, grown in this country, chiefly in Texas and extensively in India and Java. It is a very light yellow oil when properly refined, with only a faint odor when fresh. Chemically it is triglyceryl ricinoleate, and the odor of the rancid oil is due to ricinoleic acid and its oxidation products. The specific gravity at 15.5° C. is 0.96 to 0.968, and a gallon weighs almost exactly 8 pounds. It solidifies at —10° to —18° C. Its constants as follows, Saponification value 176 to 184; Iodine number 82 to 90; Acid value 0.14 for fresh oil. It has a vis-

cosity of 980 centipoises at 21° C., which makes it very suitable as a vehicle in which to grind pigment to a pigment stock. Castor oil retains its fluidity through a wide range of temperature and is therefore utilized considerably as a lubricant for airplanes and automobiles.

The blown castor oils., those that have been bodied by the combined action of air and heat, are coming into considerable use in lacquers. While not as good a softener as the raw castor oil, blown castor oil gives a much tougher film and one which permits of the use of more of the oil. Blown castor oil, either alone or mixed with varying percentages of other plasticisers such as lindol, makes an excellent vehicle in which to grind pigments on stone or roller mills.

In lacquers it is used in varying percentages. One ounce to each 4 ounces of pyroxylin is sufficient to prevent bridging but more is added if real flexibility is required. Certain leather dopes contain equal weights of oil and pyroxylin and are very flexible, although naturally quite soft. In enamels, 6 to 8 ounces per gallon are generally added though this varies with the amount of pigment, pyroxylin and gum in the enamel. The disadvantages of castor oil have been alluded to above, but it remains a widely used plasticiser in the cheaper grades of lacquers. Where a rapid hardening of the film is desired, so as to permit of packing the lacquer article, an hour or so after finishing, castor oil seems to be out of the question as it leaves the surface soft and tacky for an appreciable length of time.

### **Linseed Oil.**

This universal constituent of paints and varnishes has been the subject of so many books and articles that only a brief outline is permissible here. It is derived from flax seed and in the raw state contains certain mucilaginous materials that are removed as "foots" in the refining process. The value of linseed oil lies in the fact that it absorbs oxygen

from the air and thus dries to a moderately hard film. The speed of this oxidation is markedly accelerated by the use of compounds of lead, manganese and cobalt, which are called "driers." In small quantities linseed oil is used in the pyroxylin lacquer and in larger amounts in the artificial leather industries, but its importance is slight compared to its rank in the paint and varnish fields. Its drying qualities are comparatively unimportant as the pyroxylin film dries almost entirely by simple evaporation of the solvents, and in fact for use in such films an oil that does not dry and thus becomes brittle is considered more advisable, and castor oil is consequently used to a much larger extent.

Linseed oil has a density of 0.932 to 0.935 at 60° F., a saponification value of 189 to 195, an iodine number of about 155 and a flash point of 500° F. The color of the oil is golden yellow to greenish yellow, and a variety of bleaching processes are used to lessen the color. Sunlight is one of the best, but quicker chemical means such as oxidation with chlorine, peroxides, permanganates, etc., have been used. The oil is soluble in turpentine, hydrocarbons and esters, but sparingly so in alcohols.

To obtain rapid drying, linseed oil is often boiled, or heated with small percentages of litharge or manganese borate to about 280° C. This product, "boiled oil," dries quicker on the surface than unboiled oil, but it seems that a true drying throughout the film is not achieved any faster. A cheaper product is made by adding driers such as lead and manganese linoleates or tungates to the barreled oil.

Blown oil is made by heating with small amounts of driers and simultaneously by blowing air through the oil. This causes a partial oxidation and thickening of the material giving a product more suitable for certain inks and grinding vehicles.

Stand oil is prepared by heating to about 550° C. for a long period of time, in the presence of about  $\frac{1}{10}$  of 1 per cent of litharge and is a highly viscous, dense oil from which many

of the excellent Dutch and other European enamels are made. It is probably the best and most expensive modification of linseed oil.

Linseed oil is used in amounts up to about 5 per cent in lacquers and enamels, either the refined raw oil or good boiled oil being chosen. In leather dopes larger percentages are used, although castor and rapeseed oils are preferred in these compositions.

### Tung Oil—China Wood Oil.

This is a rather remarkable product which in the past decade or two seems to have revolutionized varnish manufacturing procedure. It is the oil of a nut grown in China, possessing a peculiar fatty smell, and of high specific gravity and viscosity. It is subject to much adulteration with soya-bean and other oils as the ultimate sources of supply, the Chinese producers, are in a disorganized condition and unscrupulous middle-men often handle the trading in the commodity.

The striking feature about tung oil is the fact that it dries not only by oxidation but by polymerization, and thus hardens at a uniform rate throughout, instead of forming a surface skin that slows down the drying of the interior as linseed oil does. The tung oil film is hard, elastic and waterproof and is thus the basis of most of the spar varnishes of to-day.

The raw tung oil requires careful treatment before it can be used, as if it is heated to above 180° C. it is liable to polymerize suddenly to a transparent insoluble jelly of no value. By heating to 160° to 180° C. with linseed oil, rosin and a few per cent of litharge it is possible to avoid this and secure an oil of the highest value for varnish manufacture. Hard fossil copals are difficult to use with it unless previously run in linseed oil, but the discovery that rosin, the cheapest of resins, and tung oil gave a varnish that equaled or surpassed the best linseed oil-copal types has had the effect of reducing markedly the demand for the expensive kauri and similar copals.

The raw oil dries flat, with a peculiar webbed or crystalline structure. This has found recent application in finishing articles like radio loud-speaker horns, as a so-called crystallizing lacquer. This is used on a baked japan or a pyroxylin enamel undercoat, and when properly applied gives a pretty, transparent crystal effect through which the undercoat shows.

Besides its high viscosity, specific gravity (0.940 to 0.945) and odor, tung oil can be detected by its reaction with a solution of iodine in chloroform, which rapidly jellifies a tung oil solution in the same solvent. The constants for this oil are very variable, but an approximate average gives an acid number of 2 to 8, a saponification value of 190 to 200, and an iodine number of 155 to 180. The oil seems to be poisonous in contact with the skin, but harmless when on walls or furniture.

The unpleasant odor can be removed in part by blowing with superheated steam, but still remains one of the greatest obstacles to a wider use of the material. The oil seems to have some field in pyroxylin lacquers as a softener, but little is known of its application in this connection. The raw oil has a tendency to give with pyroxylin opaque films of very low tensile strength or durability, but a properly processed oil might prove of value. It is soluble in hydrocarbons, ether, other oils and somewhat in esters, but is insoluble in alcohols.

Some lacquers now on the market unquestionably contain appreciable amounts of varnishes made with tung oil, with rosin or congo copal, probably thinned down after cooking with xylol or turpentine. If the proper solvents are used, most varnishes can be combined with lacquer, the kauri-lin-seed combinations giving the best results, but it is still a question as to whether such hybrids can justify their existence.

#### **Triphenyl Phosphate—Tricresyl Phosphate.**

Triphenyl phosphate was advanced as a plasticiser in 1907 by Zuhl and Eiseman in Germany. It was soon after adopted

as a camphor substitute in the celluloid industry and naturally in the pyroxylin lacquer trade. During the war the phenol from which it was made reached fantastic prices and as a result the tricresyl phosphate came into favor.

These esters are made by heating phenol or cresol with phosphorous chlorides, followed by vacuum distillation for purification. In British Patent 203,820 (1922), cresol is heated with phosphorous oxychloride and aluminum chloride to give the tricresyl phosphate. These compounds are discussed by Sachs and Byron in the *Journal of Industrial and Engineering Chemistry*, p. 893, 1921.

Triphenyl phosphate is a white to yellowish solid, melting at 49.9° and boiling at 245° C. under atmospheric pressure. Its specific gravity is about 1.25. Tricresyl phosphate is a colorless liquid, having no odor of phenos, that does not freeze but becomes very viscous at —39° C. It boils at 300° C. under atmospheric pressure, and has a specific gravity of 1.176. It has a refractive index of 1.535.

Tricresyl phosphate has almost entirely replaced triphenyl phosphate, as it seems to possess all the advantages of the latter with the economy resulting from the substitution of phenol by cresol. Under the name of Lindol this substance is sold in large quantities as a lacquer plasticiser. It can be dissolved in any of the usual lacquer solvents, gives a clear homogeneous film with pyroxylin which is not tacky under any reasonable proportion of the two components and has more plastifying effect per ounce than castor oil. The makers claim that it will overcome some of the tackiness of such gums as ester gum, and a three component film consisting of pyroxylin, ester gum and tricresyl phosphate is a common product of the evaporation of present-day lacquers. In the early days of its application as a camphor substitute, the tricresyl phosphate was prone to decompose to cresol and phosphoric acid, both of which were detrimental to the product. The present commercial article is as nearly a pure, stable substance as any in technical organic chemistry. The rate of

evaporation of Lindol from lacquer films seems to be slower than for any other plasticiser.

A great virtue of the phosphoric acid esters is the fact that they reduce inflammability. A very high percentage of lindol, say a weight equal to the pyroxylin used, will give a film that it is very difficult to ignite. The boric acid esters, such as triphenyl borate, have been proposed for similar purposes, but as far as known they are not used.

### **Butyl Stearate.**

This substance, made by esterifying stearic acid with butanol, has begun to attract some attention. It is inferior to most of the other plasticisers in its flexilizing effects, but as it is practically a wax, miscible with pyroxylin, it is used to permit of bringing up the pyroxylin surface to a high polish by rubbing or buffing.

### **Butyl Tartrate.**

Certain lacquer makers have for several years been using butyl tartrate as a plasticiser, sometimes alone, generally together with triphenyl phosphate. This compound is made by heating butanol with tartaric acid and a small amount of sulfuric acid, and purifying by vacuum distillation. It is an oily, colorless liquid, usually smelling of butanol, and boils at 203° C. at 23 mm. vacuum. Its specific gravity is 1.092 at 21° C. It contains over 97 per cent of the ester, with about 2 to 3 per cent butanol. It melts at 10° to 21° C., depending on the butanol content.

### **Dibutyl Phthalate.**

This compound, prepared by heating butanol with phthalic anhydride, is the latest plasticiser to achieve prominence. It is apparently more permanent than most of the others, that is, lacquers made with it retain their plasticity for a longer time. Its price is slightly lower than that of tricresyl phosphate. Dibutyl phthalate resembles butyl tartrate, but boils

at 212 to 215° under 37 mm. vacuum, and has a specific gravity of 1.043 to 1.05 at 21° C. It is apparently being used to a large extent in the automobile enamels now coming to the fore. The diamyl phthalate, made from amyl alcohol and phthalic anhydride has achieved some recent vogue as a plasticiser and from its chemical structure and high boiling point should be an excellent product for the purpose.

### Testing of Plasticisers.

The qualities imparted to pyroxylin by plasticisers are those of flexibility and adhesion. As an accompanying feature they generally soften the film and reduce the tensile strength, and an optimum proportion of plasticiser which will give satisfactory flexibility for its purpose without too much softening is to be preferred.

Tests for flexibility can be made by applying an enamel, usually a zinc oxide white enamel, made up with known proportions of pigment, resin, pyroxylin and plasticiser to brass plates of uniform thickness (0.015 in.). After various periods of aging these are tested by bending double over a  $\frac{1}{8}$ -inch radius. Poorly plasticised films will rupture completely, mediocre ones will show fine cracks or flake off slightly, while well-plasticised films will not be affected.

The elongation of a film, as well as its tensile strength, can be determined by preparing films of uniform thickness (0.004 to 0.006 inch) and testing them in a Suter film-tester. Marked elongation is accompanied by lowered tensile strength, and it has been found that in so far as degree of elongation is concerned, good pyroxylin lacquers are inferior to the best flexible long-oil varnishes.

The Commercial Solvents Co. test for hardness of film consists in passing metal plates coated with lacquer through sand, at a definite rate of speed. The loss in weight per unit surface per unit time is a measure of the hardness of the film. Some such apparatus as that described by Wolff (Farben Zeitung, August, 1922) might be used for the purpose.

## CHAPTER VI

### GUMS AND RESINS

Practically all of the pyroxylin lacquers and enamels now made contain certain amounts of resin. There are several reasons for this. In the first place, the resins used are usually cheaper than the pyroxylin and thus permit of obtaining increased solid concentration without unduly raising the cost. Secondly, additional resin has no perceptible effect on raising the viscosity of the solution and thus permits the securing of a lacquer of sprayable consistency containing much more solids to the gallon than pyroxylin alone. Thirdly, resin enhances the gloss, particularly of the enamels, and lastly it is of assistance in increasing the adhesion of the material, particularly to metal and glass.

The literature of gums and resins is a mass of contradictions, readily understandable when it is realized that the natural resins are collected in uncivilized countries by unscientific natives whose skill lies chiefly in cunning adulteration, that lumps of resin from the same tree may differ widely in properties depending on the length of time they have been hardening, and that methods for the analysis of resins are still in a state where the eye, nose and finger nail of a trained buyer are probably the best criteria. By far the best and most reliable book on the natural resins is that of Coffignier, entitled "Varnish" (Scott, Greenwood and Co., London, 1923), wherein many of the older data are critically revised after careful experiments by the author.

The resins used by varnish makers are generally those which when fused are soluble in linseed oil and turpentine,

while those used in the pyroxylin lacquer industry are generally the same as used in the spirit varnish industry, viz., those soluble in alcohol, esters or hydrocarbons in the cold. Such a resin, for use in lacquers, should be completely soluble in the mixture of esters, alcohols and hydrocarbons used, give a transparent mixed film with pyroxylin when dried, give a high and permanent gloss, and leave the film as hard and durable as the pyroxylin itself. No single resin known combines all these qualities.

The most widely used resins are dammar, elemi, gilsonite, pontianak, mastic, shellac and ester gum or glycerinated rosin. Zanzibar copal and sandarac gum are used to some extent, and there is a constantly increasing use of Congo and Manila copals, although the author's experience has been that these are usually very intractable in conjunction with pyroxylin in the usual solvents.

#### **Shellac—Gum-lac.**

Gum-lac is the generic term for the resin secreted by a species of insect allied to the cochineal that feed on various trees in India, Burma and Cochin China and in the course of its life processes protects itself by a covering of this waxy-resin. The twigs covered with these insects and their incrustations are called stick-lac and are treated by mixing with certain percentages of rosin and orpiment and heating in boiling water. The melted mixture is strained through a bag, and the shellac is prepared by hand labor from the melted mass, which is seized by the operator between feet, hands and teeth and thus stretched to thin sheets which are cut up into flakes. Button lac is made by pouring the melt upon green leaves and when cool resembles large ruby-red buttons. The shellac is of a brownish red color, due to a natural dye produced by the insect and for most purposes is bleached by sodium hypochlorite solutions. This gives white shellac, while unbleached material often containing some rosin and orpiment is sold as orange shellac.

A typical analysis of shellac shows, wax, 6 per cent; dye, 6.5 per cent; resin, 74.5 per cent; water, 3.5 per cent, and residue 9.5 per cent. Shellac has an iodine number of 16, a saponification value of 212, and an acid number of 50 to 60. It softens at about 60° C. and melts at 120° C. Alcohol, either ethyl or methyl, is the best solvent for the resin, although the wax is largely insoluble therein and thus causes the cloudy appearance of ordinary shellac solutions. For most purposes this cloudiness is unimportant, as the wax and resin form a clear transparent film on drying. Shellac is the best of the resins used in spirit varnishes on the score of hardness, flexibility, permanence of gloss and adhesion. It is quite expensive, costing more per pound than pyroxylin, but this is counterbalanced by the fact that its solvents, the lower alcohols, are cheap. Many imitation shellacs are on the market consisting of ester gums or cheap copals in alcohol or benzol but although they have a field of usefulness they are far inferior to true shellac.

A shellac film when sprayed is apt to acquire a pitted surface, it will soften on a rather warm day and is very susceptible to whitening on contact with water. To minimize these defects a combination lacquer consisting of pyroxylin and shellac can be used. A good formula consists of a 32-ounce low viscosity pyroxylin dissolved in ethyl acetate, 1 pint; butyl acetate, 2 pints; denatured alcohol, 5 pints, to which is added slowly with constant stirring an equal volume of a 4-pound cut of shellac in denatured alcohol. This mixture when sprayed gives a film combining the virtues of both components.

The procedure involved in dissolving shellac, as well as other resins, is essentially that of the spirit varnish maker. The resin and solvent can either be mixed in a revolving wooden or steel barrel provided with mixing arms which is rotated at about 40 R.P.M. for 6 to 8 hours, or in a stationary wooden or enameled tank provided with a mechanical agitator. The former is preferable, for on the first mixing

resins generally gelatinize with the solvents and form a mass that impedes the action of the agitator blades and sometimes breaks them. In either case, the solutions are pumped off into clarifying tanks and allowed to settle, are filtered, or centrifuged. The first method requires least initial expense, but involves considerable tied-up capital and does not lend itself to rapid production. Filtration is tedious in many cases due to the slimy residues, and the volatility of the solvents used. The centrifuge seems by all odds the best method for clarifying resin solutions as well as pyroxylin solutions and it has been adopted by many of the leading lacquer manufacturers.

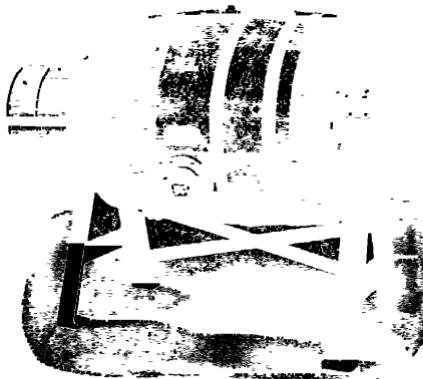


FIG. 1.—Gum and resin dissolver.

It will be discussed later under pyroxylin solutions. (Figs. 1 and 2.)

Commercial shellac generally contains 2 to 5 per cent of rosin, but occasionally it is sophisticated by gross addition of this cheap resin. A good test for rosin addition is the Storch-Marewski method. One gram of shellac is added to 15 c.c. of acetic anhydride, warmed till dissolved and then cooled. Most of the shellac separates out as a gelatinous precipitate and is filtered off. The filtrate is placed in a test tube, slightly inclined and two or three drops of concentrated sulfuric acid allowed to flow down the side. At the juncture of the two liquids a red to violet coloration appears in the

presence of two or three per cent of rosin, and with practice a fairly close estimation can be made by means of the depth of color. The acid value is another indication, for rosin has a high acid number which will raise that of the shellac appreciably if present in any considerable percentage.

For use in pyroxylin lacquers a specially treated shellac is now on the market. It is rosin-free, refined, bleached, bone-

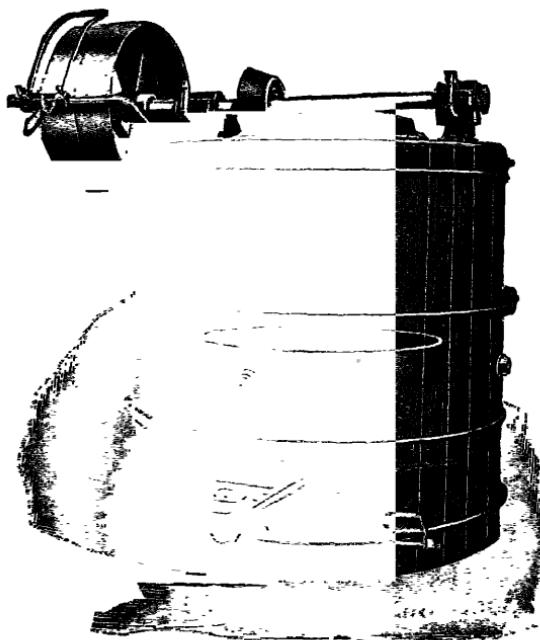


FIG. 2.—Gum and resin dissolver.

dry and wax-free. Its price is much higher than that of pyroxylin, but where high grade lacquers are to be made it is an excellent resin. This commodity softens at 90° C. and has a bulking value of ten pounds to a gallon.

A great disadvantage of shellac is the fact that it is but slightly soluble in the esters and hydrocarbons that predominate in lacquer formulae. This and its cost have restricted its use to special formulae that are rather expensive, not only

because of the cost of the shellac itself but of the high boiling alcohols that are incorporated into the formula to take care of it. A coat of shellac in denatured alcohol is often used, however, as an undercoat for pyroxylin materials. In such a case as where it is desired to enamel wood containing either a natural dye or previously applied soluble stains, it is often found that the dye or stain dissolves in the lacquer solvents and bleeds through and discolors light-colored enamels. If a coat of shellac be first applied, two benefits are obtained. The pores of the wood are filled, and, since the shellac solution is a non-solvent for the wood dye, and the shellac itself insoluble in the usual lacquer solvents this discoloration is prevented. Some finishers prefer to use a bronzing liquid containing aluminium powder to achieve the same result, but better results are usually obtained with shellac.

The same procedure is often used where it is desired to refinish with pyroxylin products objects that have previously been coated with oil and resin materials.

### Dammar.

Dammar gum is an exudation from *Shorea* trees in Malaysia, which has hardened more or less by exposure to the air. Dammar in Malay signifies "torch," and the name was given because it was used as an illuminant before its value in varnishes and lacquers was realized. The Batavia and Singapore dammars are those used almost exclusively in the lacquer trade, and can only be distinguished from each other by careful examination. They are among the palest and whitest of all resins and for this reason are used largely in white enamels and colorless lacquers. In the trade they come as white to yellowish white lumps of various sizes mixed with dust resulting from the attrition of these lumps on each other, and an appreciable amount of dirt.

Batavian dammar has a density of 1.103 and an acid number of about 35.5. It melts about 100° C. The resin is very brittle and the lumps can be broken between the fingers, while

it does not give a gummy mass when chewed and is thus differentiated from mastic. On rubbing a slight aromatic odor is perceived. The Singapore dammar resembles the Batavian variety very closely, but has a density of 1.057, an acid number of 30 and a melting point of 95° C.

The dammars dissolve almost completely in benzol, chloroform, ether and amyl acetate and only partially in alcohols. This is due to the fact that dammar, like shellac, consists of both wax and resin and the wax is insoluble in alcohol. Solutions of dammar in benzol or turpentine with or without amyl acetate and fusel oil have been used considerably as a cheap, quick drying and almost colorless varnish. The tackiness of the film, together with its habit of crumbling when rubbed or scratched, makes it usable only where no wear is expected to be encountered.

When attempting to dissolve dammar and use the solution together with pyroxylin it was found that while a benzoldammar solution was quite clear and deposited a clear film, a mixture of this with a pyroxylin solution gave films that were cloudy and sticky, due to the wax which apparently does not form a homogeneous solid solution with the resin and pyroxylin. It was found necessary to free the solution from the wax, and a number of formulae exist for this purpose. A typical one consists of dissolving 10 pounds of pulverized dammar in a gallon consisting of 15 per cent ethyl acetate, 15 per cent acetone and 70 per cent benzol and then adding  $\frac{3}{4}$  gallon of wood alcohol. The wax is thus precipitated as a gray, slimy, stringy mass which is allowed to settle and the clear solution drawn off. This solution will give unclouded films with pyroxylin and is probably next to shellac the best resin solution that can be added for light-colored products. About 20 to 25 per cent of the dammer is lost as wax, which is generally burned after accumulation of sizable quantities. Assuming 25 per cent lost, and a bulking value of 9.5 pounds to a gallon for dammar it can be calculated that the above solution contains about 3 pounds of resin in a gallon. In all work

with resins it is well to distinguish between "pounds to a gallon" and "pounds in a gallon." The former means the number of pounds of resin added to a gallon of solvent, and the latter the actual solid contents of the solution after allowing for the expansion due to solution and the insoluble matter contained in the resin. The latter value can be determined by dividing the number of pounds taken to a gallon by 1 plus the weight taken divided by the bulking value of the resin. The bulking value can be found by multiplying the density of the resin by 8.33, the weight of a gallon of water in pounds.

In practice the determination is best made by analysis. One liquid ounce is poured into an aluminum box of about 2 ounce or 60 c.c. capacity, previously weighed, the box covered by a piece of filter paper and placed in an oven at about 80° for 2 hours. After cooling the box is weighed and the amount of solid determined by difference. This value, in grams as generally obtained, when multiplied by 128/453 or 0.2825 gives the value in pounds to a gallon.

Since the light color of dammar is its chief merit care must be exercised in dissolving and stirring the material to avoid discoloration. Metals such as iron and to a lesser extent copper and brass are attacked by dammar solutions sufficiently to give a yellowish, reddish or green color to the solution. The dissolving is best done in wood or enameled metal tanks or rotating churns, and storage in steel tanks lined with tin or lead is recommended. Dammar is used in lacquers up to twice the pyroxylin content, more than this generally giving too soft a film. The gloss given by dammar has a tendency to diminish on standing but can be preserved by a coat of clear lacquer over it.

### Zanzibar Copal.

It is claimed by one manufacture of lacquers that he utilizes Zanzibar copal in his products, using a processing method so far kept secret. Its advantages as a varnish gum do not

seem to be so marked in conjunction with pyroxylin. Zanzibar copal, or gum animi, is one of the most valued varnish resins because of its hardness and durability. In varnish making it is heated to about 300° C. and about  $\frac{1}{6}$  of the material volatilized off, leaving a residue that dissolves readily in linseed oil and turpentine. In the cold the solubility of the copal is low in any of the usual lacquer ingredients, and it is the author's belief that any incorporation of it with lacquers must imply a preliminary fusion, possibly followed by esterification of the pyrocopal with glycerine. Zanzibar copal is found as a fossil gum in Africa, and comes to the market in irregular lumps characterized by a goose-skin crust. The density of this copal is 1.06 to 1.13 when powdered and the air in the cavities thus eliminated. It has a melting point of 280° C.

#### Congo Copal.

This is a softer, more fusible and cheaper resin of markedly superior solubility. It resembles the Zanzibar variety, with the exception that it does not possess the goose-skin wrinkled surface. Congo melts at 220° C., but begins to soften at 140° C. Cold absolute alcohol dissolves it almost completely, as do ether, amyl acetate and fusel oil.

#### Kauri Copal.

This variety, found in New Zealand, is an amber to light yellow resin of a density of 1.109 to 1.115. It melts at 165° C. and has an acid number of 70.9. It is quite soluble in amyl acetate, alcohol and ether mixtures and slightly less so in acetone.

#### Manila Copal.

This is the cheapest copal, as well as the most fusible. It melts at 120° C., softening at 103° C. It dissolves readily in alcohol, fusel oil, amyl acetate, etc.

The copals, even in solution, make poor resins for use in pyroxylin lacquers. A solution of say Kauri copal in fusel oil, mixed with a pyroxylin solution in amyl acetate has a tendency to give a system with two layers, and the film resulting on drying is not only of poor hardness and adherence, but is cloudy. Manila copal has the additional disadvantage of giving stringy gelatinous masses when used with some pigments in enamels, as well as imparting its own peculiar property of coming off in long strings when the film is pulled after being apparently dry and hard. They are used to only a slight degree in lacquers for these reasons, though it may be possible that by proper heat treatment or esterification they will some time be made usable.

### **Elemi Gum.**

This differs from the previously considered resins in being an oleo-resin, that is a mixture of resin and essential oils. It comes from various parts of the world, but that used in pyroxylin lacquers is generally the soft Manila variety, found in the Philippine Islands. It is generally sold in 80-pound tin cases, and resembles a soft wax in consistency and glue in stickiness. It has a pleasant balsamic odor that clings tenaciously to the film. Elemi softens at 0° C., and melts at 120° C. At all ordinary temperatures it gives a sticky, tenacious film that dries very slowly. Elemi is almost completely soluble in benzol, alcohol and ethyl acetate. The color is white, with a yellow or greenish tinge. The density is 1.085. Commercial elemi contains much woody fiber and other impurities owing to the difficulty of cleaning the sticky mass. The use of elemi in spirit varnishes and in pyroxylin lacquers is due to its property of retaining flexibility for a long period and imparting this property to other gums and to pyroxylin. In any considerable percentage elemi leaves the film entirely too soft so care must be taken in its use.

Elemi is generally dissolved in wooden vats, provided with a close fitting cover and an agitator. The solvents vary, but

one consisting of ethyl acetate, 25 per cent, alcohol, 20 per cent, and benzol, 55 per cent, has been found to give good results. When dissolved, the yellowish to orange solution is allowed to settled for 24 hours and the clear solution remaining after the subsidence of mechanical impurities and slight undissolved amounts of the oleo-resin is pumped off into storage tanks. Six pounds of elemi to each gallon of solvent is the proportion generally used. The handling of the sticky gum is troublesome and it has been found of advantage to open the top and one side of the tin case and scoop the resin into the solvent with a wooden paddle. Some importers of elemi pack their goods in tin cans lined with paper, by far the preferable form in which to secure the gum.

The elemi solution made as described is generally used in proportions of 5 to 15 per cent by volume of the pyroxylin solution. It increases adhesion and flexibility, but decreases hardness. Some bronzing liquids, especially those used for chandelier chains and other articles that must be bent or sheared after lacquering use rather high percentages.

### **Pontianak Gum.**

This resin is found in Borneo, and has achieved some use in the pyroxylin industries. The lower grades are somewhat cheaper than dammar but the best pale Pontianak is more expensive. The resin has a specific gravity of 1.037, an acid number of about 20 and a melting point of 135° C., although it begins to soften considerably below that temperature.

Pontianak is soluble in ethyl acetate, acetone, fusel oil, amyl acetate, benzol and anhydrous alcohol-ethyl acetate mixtures. Six or eight pound cuts are usually employed. The solutions have a yellow to reddish orange color.

### **Sandarac Gum.**

Sandarac would probably be used to a greater extent if the supply were more regular and abundant. It is a fairly

hard, not readily fusible resin, soluble in alcohol, fusel oil and ether and slightly soluble in benzol. The standard resin comes from Africa, but an Australian variety is known. It has a specific gravity of 1.038 to 1.044 and a melting point of 150° C. Owing to its peculiar property of drying to a frosted surface from a solution in alcohol and benzine, it has been used to give an etched or ground glass effect to glass electric bulbs, etc., having the advantage over hydrofluoric acid etching that the material can readily be removed.

### Mastic.

The resin is distinguished by giving a coherent elastic mass when chewed, and is the original chewing gum. It is still used to replace chicle to some extent. Mastic comes almost exclusively from Chios, a Greek island, and is used to a limited extent in pyroxylin lacquers.

It has a specific gravity of 1.05 to 1.06, softens at 100° C. and melts between 105° and 120° C. It is soluble in turpentine, acetone, alcohol and fusel oil. It is claimed by some users that a desirable plasticity and flow is imparted to lacquers in which mastic is used.

### Dissolved Copals.

The manufacturers of the absolute alcohol-absolute ethyl acetate solvent used for dissolving the A. S. pyroxylin have recently placed on the market solutions of the popular resins in the same solvent for use in conjunction with the former material. Kauri, Pontianak and Congo copals are procurable in 6 to 8 pound cuts, the last named being the cheapest and most widely used. The smaller lacquer makers find an advantage in securing their resins already processed and dissolved, but it is more economical for the larger users to save the handling profit, and cut and filter their own resins.

### Gilsonite.

While not strictly a resin, gilsonite is used rather widely in the lacquer industry and can best be considered in this chapter. It is a fossil bitumen, resembling coal tar pitch in its appearance, brittle, of a hardness 2 in the mineralogical scale and of a glossy black color on freshly fractured surfaces. It has a density of 1.043 to 1.046, melts at 123° C. and is completely soluble in benzol to the extent of 4 pounds to a gallon. Gilsonite has found use in black lacquers, both flat and gloss, as it gives an addition of body and of color at the same time. Although black in the solid state a solution of gilsonite is a dark brown, and in gloss black lacquers it is tinted up with nigrosine or similar dyes, while in the flat blacks the effect is obtained by mixing lamp or carbon black, previously ground in oil or pyroxylin, with it. The use of gilsonite, which is very cheap, permits of economies in several ways. Some of the pyroxylin required to give body is replaced, some of the resin used to give gloss also substituted and a certain amount of the expensive dye or fine black pigment can also be replaced by this substance. The finest black lacquers do not contain gilsonite, however, as it does not leave as hard or durable a film as certain other combinations.

### Synthetic Resins.

Of the many synthetic resins produced in the endeavor to make an artificial product that would compete in price and quality with natural ones, only one has found extensive use in lacquers. This is ester gum, and, strictly speaking, is not a synthetic product, for the rosin from which it is made is produced only by nature. However, since it is made from rosin by a chemical process, ester gum is generally classed as an artificial resin.

Rosin is the raw material, and is the cheapest and most abundant resinous substance. It is derived from the crude turpentine, or sap exudate from certain species of pine and

other coniferous trees, by distillation. The rosin is valued according to its color, which varies from almost glass-like transparency and colorlessness to very dark amber. It has an acid number of 160, a saponification value of 174 and an iodine number of 168. It has a density of 1.08 and melts between 100 and 140° C.

Since rosin consists almost entirely of an acid (abietic acid) and its anhydride, it is unsuitable in itself as an ingredient of lacquers, although solutions of rosin in benzol are sold in some quantity to the very cheapest trade. The acid not only attacks metals, but reacts with many pigments to form compounds that thicken and ruin the enamel. For some purposes rosin is freed from acid by heating with lime, zinc oxide, etc., which react with it to give metal abietates and reduce the acidity to usable limits. These products, however, do not give clear films with pyroxylin. The process of making ester gum consists in treating rosin with a high-boiling alcohol, generally glycerol, which unites with it to give glycetyl abietate. Enormous quantities of ester gum are being made and sold to the varnish and lacquer trades under various tradenames such as Glycro-ester or Paramet, and is used more than any other resin in the lacquer industry.

The process for making Ester Gum for the varnish industry is theoretically simple, but most manufacturers have found it to their advantage to purchase the material from firms specializing in its production. A typical run consists of melting 600 pounds of pale rosin in an aluminum kettle at 400° F., adding 72 pounds of glycerol and then raising the temperature to 550° F. for 20 minutes. The kettle is provided with a condenser so arranged as to permit the glycerol vapors to condense and run back into the kettle, while the water formed in the reaction escapes as vapor. After the fusion and esterification are complete 3 pounds of powdered lime are added and after 10 minutes the fused material is poured into barrels to harden. It must be understood material made with lime is not as suitable for lacquers as that made with glycerol alone.

to which class belong the brands of ester gum mentioned above. These are made for the lacquer trade of rosin and glycerine alone, of varying degrees of hardness, acidity and color.

By this process the acid number of the rosin is reduced from 160 to 10 or less. Complete neutrality could be secured by using more glycerin, but it would entail the possibility of some glycerin remaining in the material with consequent tackiness. The material is pale in color and resembles the original rosin very closely. It is very soluble in benzol, toluol and turpentine, leaving no residue besides occasional wood fibers from the barrels in which it is packed. It is insoluble in 80 per cent alcohol. Ten pounds of ester gum bulk to one gallon.

Ester gum is unaffected by hot or cold water or dilute sodium carbonate solutions. It is hydrolyzed by hot alkalis. Properly made, it does not possess the burnt odor characteristic of overheated rosin. It is the cheapest resin used in the lacquer industry and the one most widely used.

For use in pyroxylin lacquers it is generally dissolved in the proportions of 6, 8 or 10 pounds to a gallon in either the rotating or stationary mixers described under shellac. As solvent some manufacturers use benzol, or mixture of benzol and toluol. Such solutions, however, have a tendency to cause local precipitation of pyroxylin, and it is recommended that the ester gum be dissolved in such mixtures as 25 per cent ethyl acetate and 75 per cent benzol. Solutions of ester gum can easily be filtered and this practice is advisable to prevent incorporating mechanical impurities into the lacquer.

Ester gum can be used in lacquers in proportions ranging to three-fourths the weight of pyroxylin. Larger quantities tend to give soft, easily removable films. If more gum is desired in the solution, dammar or shellac is added. In gloss enamels, where additional hardness is given by the pigments themselves, ester gum can be used in proportions up to twice the weight of the pyroxylin.

The gum should be tested for acidity, by dissolving in

benzol and applying to the brass strip as previously described No discoloration should appear. Twenty-five per cent of the solution when added to 75 per cent of a 16-ounce pyroxylin cut in 25 per cent butyl acetate and 75 per cent toluol, should give a clear, transparent film that dries without tackiness in one hour. The color of a 6 pound cut should not be darker than light amber. This color, by the way, is intensified by contact with iron, and ester gum solutions should be stored in tinned or white metal lined containers.

### Cumarone-Indene Resins.

Cumarone and indene are found in the high boiling fractions of coal-tar naphtha, generally in that portion boiling between 160° and 180° C. When these are heated with small amounts of sulfuric acid or aluminum chloride a polymerization takes place and resins are formed which are competing strongly with ester gum in the varnish and, to a much lesser extent, in the lacquer trades.

These resins resemble rosin in appearance, but differ greatly in chemical composition. They are neutral, and have practically zero acid and saponification numbers. They dissolve in esters, oils and hydrocarbons, but are insoluble in alcohol. The density varies from 1.05 to 1.15.

The chief American brand is made in 5 grades, classified according to their melting point. The varnish grade melts from 127 to 142° C. The color ranges from a very light yellow to a dark amber. These resins cost approximately the same as ester gum, thus being among the cheapest of resins.

### Phenolic Condensation Resins.

The most promising source of synthetic lacquer resins seems to lie in the domain of the condensation products of phenol, or carbolic acid, and aldehydes such as formaldehyde. This is the reaction that produces the well-known bakelite, and is susceptible of wide modification with corre-

sponding variations in the nature of the product. Changes in proportions, in catalysts, and in the temperature, pressure and time employed seem to permit of the manufacture of resins with almost any desired characteristics.

For several years spirit-soluble phenol-formaldehyde resins were used abroad under the name of Albertols to replace shellac. They were far from satisfactory for the purpose. Another type of Albertol, wherein natural resins such as rosin are combined with the condensation product, was also developed, primarily for the varnish industry to replace the natural copals, with better success. These so-called Kauri Albertols, however, had poor color, darkening under fusion, and limited solubility in varnish oils and poor compatibility with nitro-cellulose.

Recently, however, the manufacture of this type of synthetic resin under the patents of Dr. Kurt Albert, inventor of Albertol, has been commenced in this country. A greatly improved product, in which most of the previous drawbacks have been eliminated is being made under the name of "amberol," and is finding a constantly increasing use both in varnish and lacquer.

The amberol BS is best dissolved in coal tar hydrocarbons, such as toluol, with the addition of about 10 per cent of butyl acetate. It gives solutions that are more viscous than rosin or ester gum cuts of the same concentration and an 8 or 10 pound cut is about the heaviest used. In appearance the amberols resemble rosin or ester gum, but they are much harder, less fusible, and possess greater lustre and durability to exposure in both varnish and lacquer films. The solid gum and its solutions have a peculiar fluorescence, which does not seem to be transmitted to the finished product.

The solvent mixture in the lacquers to which amberol is added must be correctly balanced to avoid a clouding up of the film. Any cloud can generally be eliminated by the addition of butanol or amyl alcohol; small amounts of linseed oil and xylol have been found helpful. The films produced from

mixtures of amberol pyroxylin and plasticiser have been found to possess high lustre that does not dull rapidly, as does that obtained with ester gum, excellent resistance to exposure, and marked hardness. At present prices, amberol is more expensive than ester gum, but is about as cheap as dammar seeds, when the loss in dewaxing the dammar is considered. The time and labor consumed in making an amberol solution is much less than that required for dammar and the color, while appreciably higher than Batavia No. 1 dammar, is about equivalent to that produced with dammar seeds or dust. For pure white or colorless lacquers it is still not wholly satisfactory.

It is greatly to be hoped that American-made synthetic resins will be developed that will in time wholly displace the imported shellac, kauri, dammar and other resins. Every ingredient in lacquer, with the exception of the natural resins, is produced in this country; the resins on the other hand are subject to the whims of both factors and natives in the tropics, the supply is uncertain, and the price varies within wide limits. With the amount of research going on in the field, not only in the above type of product but in the glycerine-phthalic acid and urea-formaldehyde resins, this desirable result seems certain to occur.

The amberol BS<sub>1</sub> melts at 95°-105° C., has an acid number of 15-22, and dissolves in hydrocarbons, amyl acetate and butyl acetate. It darkens only slightly on exposure.

Amberol H<sub>9</sub> is slightly softer, more compatible with pyroxylin and cheaper.

## CHAPTER VII

### PIGMENTS AND DYES

Lacquer enamels are essentially lacquers in which pigments or dyes have been incorporated so as to give the desired color. Probably no phase of the pyroxylin lacquer industry is in so unsatisfactory a condition as the choice of pigments, despite the enormous amount of work and accumulated data on the subject of these coloring materials in the hands of the paint and varnish manufacturers. Paint formulae and specifications offer poor guides for lacquer enamel manufacture, inasmuch as the vehicle differs so widely from those used in these products. For instance, a linseed oil paint may contain 6 pounds or more of pigment to a gallon, while an attempt to incorporate anything like that amount into an average lacquer formula would lead to a product of practically no durability, adhesion or value. This is due to the low percentage of non-volatile matter in the lacquer compared to paints or oleoresinous varnishes, which means a much lower percentage of binder for the pigment. Different pigments are thus indicated for use in lacquer; the fact that white lead, which is the painter's touchstone, is scarcely used at all in the lacquer industry giving some indication of the differences encountered. Pigments have been chosen hitherto for their workability in an oil medium under the brush, and now a vehicle of low body, different index of refraction and entirely different method of application and drying is to be used. Previous experience is only of minor use in this connection and the choice of pigments to secure maximum coverage, opacity, durability and economy is still in a condition where much research

work from the ground up is necessary. Manufacturers so far have begged the question by using high strength C. P. colors, regardless of expense; and present lacquers are predominatingly composed of such high strength pigments as carbon black, zinc oxide and titanox whites, toluidin red, prussian blue, C. P. chrome green, etc. From a few ounces to between 2 and 3 pounds of pigment per gallon are used. The question of the use of extenders, not only to cheapen the product, but to better it, remains to be investigated thoroughly, but it is certain that as competition becomes keener cheaper pigments will be used, and probably to good advantage. New pigments designed especially for use in conjunction with pyroxylin will undoubtedly appear, and others that have been discarded for use with oils owing to their inhibiting effect on drying, or too low oil-absorption factor or for similar reasons may be found excellent for use in lacquer enamels.

Volumes can be and have been written about pigments and their manufacture, so there is scope in this volume only for a brief survey of the natural and artificial pigments which are of the most importance to the pyroxylin lacquer industry as constituents of enamels, fillers and glazes. Although the number of pigments is legion, those actually used to any marked extent are very few. The most important by far are the white and black pigments, with blue, green, yellow, red and brown in the order named.

### WHITE PIGMENTS

#### Zinc Oxide

Until quite recently the pigment used almost exclusively for the production of white lacquer enamels was zinc oxide, the French Process White Seal type being especially favored. This is one of the purest and whitest of pigments and was adopted mainly for the reason that it would almost certainly work without requiring tests extending over several years. Zinc oxide is made in two ways. The first, or direct process,

uses natural ores of zinc, particularly franklinite. The ore is mixed with anthracite coal in a closed retort, the retort heated to a point above the volatilization temperature of zinc, and the vapors of the metal after mixing with air are burnt to the oxide which is collected in a series of bags in a bag-house. The coarser particles settle in the bags nearest the retort, the finer in progressively distant containers. This type of pigment contains some lead compounds and is considerably cheaper than the French process material. It is used widely in paints, but only to a slight extent in lacquer enamels.

The French process is somewhat similar, but the raw material is pure zinc or spelter. The product is air or water floated, bolted, and otherwise classified in the order of fineness. The white seal is the best and most expensive, but the green and red seal products are also used.

The density of zinc oxide is about 5.6 and the bulking value is 46.7 pounds to a gallon. In other words, for every 46.7 pounds of zinc oxide incorporated into a lacquer one gallon of volume has been added. The pigment is permanent in the air and sunlight, is resistant to sulfur fumes, but in oil paints and varnishes has a tendency to become hard and brittle with age. This was overcome by the addition of 10 to 25 per cent of white lead. This characteristic does not seem to be evident in the lacquer whites, probably because more attention is paid to plasticising them.

The color of the best zinc oxide is probably as near a true white as can be obtained, although a slight bluish tinge is often met with and is generally not objectionable, as it tends to neutralize some of the yellowness of the oils and gums in the vehicle. The color is tested by adding one part of Prussian blue to 100 parts of the zinc oxide, and one part of chrome yellow to another 100 parts, stirring them to homogeneous pastes with turpentine and noting the resulting colors. The blue should give a true bluish white, the yellow a true yellowish white, with no greenish tinge in either case. The presence of lithopone is detected by adding a few drops of hydrochloric

acid to a few grams of the pigment and holding over it a strip of paper soaked in lead acetate solution. A blackening indicates the presence of the cheaper lithopone. White lead can be detected by placing some of the pigment on a piece of filter paper and exposing it to the vapors of hydrogen sulfide or ammonium sulfide. A blackening indicates the presence of white lead. Zinc oxide should dissolve completely, and without effervescence in moderately concentrated hydrochloric acid. No other white pigment does this.

Although the density of the pigment is high, the white seal material is so fine and contains so many air spaces that its dry bulking volume is large. This causes some trouble in pebble-mill grinding, as it is difficult to introduce the full amount called for by the capacity of the mill and the formula without two fillings of the mill. If part is first introduced and ground into the vehicle for a short period, room is made for the rest of the required material.

A great advantage of zinc oxide over white lead and lithopone is its chemical stability. It does not blacken with ultramarine, as white lead does, nor does it blacken lead or copper pigments such as chrone yellow or verdigris as does occasionally lithopone. The sulfide of zinc is white, and this makes the action of sulfur fumes unnoticed. Titanox is at least as stable, and so is barytes, but the latter is not strictly a pigment.

The hiding power or opacity of zinc oxide is inferior to that of the other white pigments to be considered and it is for this reason that it is being gradually replaced by lithophane and titanox pigments wherever possible.

### Lithopone.

The use of this pigment is increasing very rapidly in recent years, although for many years after its discovery in 1874 it was not considered to be of high quality as a pigment. Much of the opposition was due to the habit the early product had of blackening markedly in bright sunlight, a tendency which restricted its use to interior work and made most paint manu-

facturers skeptical of its other merits. Its low price and high coverage made it in demand and continual research work has brought up its quality to a point where this darkening has been obviated almost completely and lithopone is now replacing zinc oxide in almost all formulae where lead, copper, and iron are absent.

Lithopone is a composite of zinc sulfide and barium sulfate, made by precipitating solutions of zinc sulfate with barium sulfide. The barium sulfide is made from the crude barytes as mined in Missouri and elsewhere by heating in the absence of air with bituminous coal and salt. It is then digested, filtered and brought to the proper concentration. Scrap zinc is dissolved in sulfuric acid, and the resulting zinc sulfate solution also concentrated. The two solutions are heated to 140° to 150° F. and mixed, the zinc sulfate being added twice as fast as the barium sulfide solution. The resulting precipitate is filtered off, dried, and the filter cakes heated to 900° F. and then suddenly plunged into cold water. The product is then ground to a pulp with water, washed with 10 to 15 changes of water to remove excess salts, filter pressed, dried and disintegrated to the required fineness after which it is packed in barrels for shipment. The final product averages 30 per cent zinc sulfide, 1 to 2 per cent zinc oxide, and the rest barium sulfate. The density varies slightly, but is about 4.25 and the bulking value is 35.4 pounds to the gallon.

The white given by lithopone of good grade is quite comparable to that of the best zinc oxide, its hiding power is considerably better, it stays longer in suspension, and since it has a greater apparent density, i.e., fewer air spaces, it can generally be mixed with the vehicle in one filling. Its price is about one half that of the white seal zinc oxide and with its lower bulking value and consequent greater expansion it affords another slight economy.

Lithopone should be water free, and this can be determined by heating a weighed amount in a porcelain dish at 110° C. for 4 hours, and noting the loss in weight if any. Its suscepti-

bility to light is best determined by rubbing up a few grams with enough pale dammar solution or 8-ounce pyroxylin solution to give a paste, spreading this paste on a porcelain tile or zinc-white enameled board and exposing to the sunlight for several hours. No darkening should occur. It is claimed that this is better shown by making the paste with water, which apparently accelerates the reaction. However, it is now safe to assume that the product sold as light-fast lithopone by the reputable makers is actually light fast. The only adulteration that might be found is the replacement of some of the zinc sulfide by barytes, whiting or other inferior pigment. This can be determined by digesting with 6N hydrochloric acid, filtering, adding sodium acetate and passing hydrogen sulfide through the solution. The precipitated zinc sulfide is weighed and from the weight of sample taken the percentage of zinc in the original material can be found. Details of this and other standard methods of determining zinc can be found in any good textbook of analytical chemistry.

### **High Strength Lithopones.**

Recently lithopones having 50 per cent or more of zinc sulfide have been made which have a coverage markedly greater than ordinary lithopone, in fact approximating titanox in that respect, and since they are cheaper than titanox they are finding a definite place in the field. The practically pure (96 per cent) zinc sulfide is also on the market now as a white pigment, and while considerably more expensive even than titanox, its hiding power is so great that for many purposes it is favored. By virtue of its hiding power and the correspondingly lower amount of pigment needed, a higher gloss is obtainable and less binder needed. It is understood that this material is made by heating zinc oxide with sulfur.

### **Titanium Whites.**

Titanium was long considered one of the rare metals and its compounds were only of academic interest until recently.

New sources of this element and methods for treating the ores have been developed that permit of the production of pigments with titanium as a base that are cutting heavily into the zinc oxide and lithopone industries. Under the name of "Titanox" a titanium pigment has come into prominence which in opacity, inertness, and bulking value seems to be superior to any of the other pigments and whose price is only slightly higher than the best zinc oxide.

Titanox is a mixture of titanium oxide and barium sulfate, prepared by treating a solution of titanium sulfate with barytes, evaporating and hydrolyzing with live steam. It has a density of 4.3 and a bulking value of 35.8 pounds to a gallon. These constants are practically those of lithopone, over which titanox has the advantages of opacity and inertness. The chemical composition of titanox is 25 per cent titanium oxide and 75 per cent barium sulfate, and it is sold under these specifications. It does not alter in the light, and is chemically inert to all pigments and ordinary atmospheric gases. The makers claim that its opacity is nearly double that of zinc oxide and about 25 per cent greater than that of lithopone. Two advantages follow from this, a more opaque enamel can be made with the same weight of pigment, and an opacity equal to previous lithopone or zinc oxide enamels can be obtained with less pigment, and thus permits of a thinner film being applied with consequent economy.

The pure titanium oxide is also used as a pigment, but its cost is out of proportion to its superiority over titanox.

The chief objection to titanox is the part that occasional batches are yellowish. This can be overcome by the use of small amounts of blue pigment.

#### **Antimony Oxide—Timonox.**

This white is produced by burning the stibnite mineral of commerce and is a brilliant white pigment that has some vogue as an ingredient in special paint and enamel mixtures. So far as known it has no application to lacquer enamels, but it may

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solve some special problem and is therefore mentioned. Its density and bulking value are approximately the same as zinc oxide, its price is lower, and since it is not susceptible to the action of sulfur fumes, it is used abroad in paints for gasometers, factories, coal mines, etc.

**Barytes—Blanc Fixe.**

These pigments are chemically identical, consisting almost entirely of barium sulfate. Barytes is a crystalline form obtained from natural barytes by careful grinding, washing and classification, while blanc fixe is an amorphous variety prepared by precipitating a solution of barium chloride with sulfuric acid. In opacity these pigments are far inferior to those previously mentioned and are thus never used alone. They have considerable value as "extenders" or fillers, especially where pigments of very high opacity or tinting strength are used. For instance, 100 per cent titanox is only slightly superior to the commercial variety, which is 25 titanium oxide and 75 per cent blanc fixe, and 100 per cent chromium oxide green covers only slightly better than one containing 20 to 30 per cent of the green and the rest blanc fixe. The cheapness of these materials thus permits of marked economy in many cases. Blanc fixe is far more effective than barytes but costs several times as much. It is the preferred form for high grade products, the latter being used in the very cheapest paints.

The density of these pigments is 4.16, and the bulking value is 34.7 pounds to a gallon. They may contain traces of iron, which would yellow any white with which they are mixed, and it is well to rub a sample up with turpentine and permit to dry next to a similarly treated sample of known zinc oxide to detect this. They are not very easy to grind in the usual roller or stone mills.

**Whiting.**

This is essentially a pure, finely ground, limestone or calcium carbonate. It is very transparent, and is thus used only

as a filler. Whiting comes in many grades, but the fine gilder's whiting is the only one worth using in a lacquer enamel or filler, although the coarser grades serve for the making of putty and knifing glazes. Whiting neutralizes traces of free acid and is thus a valuable ingredient in many cases, but enamels containing it are liable to pit when exposed to any high concentration of acid fumes or liquid. Its widest use is in rough stuffs, wood fillers and knifing putties, where it has very excellent filling and adhering properties. Its alkalinity, due to traces of lime, makes it objectionable with such colors as prussian blue and chrome green.

Whiting has a density of 2.7 to 2.85 and a bulking value of 23.35 pounds to a gallon.

#### Silica—Silex.

Both of these pigments are silicon dioxide, silica being derived from quartz and silex from flint. The raw material, after being freed from iron and other impurities by an acid wash is finely ground and air or water floated. The density ranges from 2.18 to 2.5, giving bulking values of 18.18 to 20.85 pounds to a gallon. These pigments are absolutely inert, and almost completely transparent. The last quality renders them useful in wood fillers where it is desired to fill the pores of the wood without obscuring the grain. One unusual feature of silica is its gritty feel even when finely ground, and this property is connected with its so-called "tooth" or gripping power on surfaces, which power silica has to the highest degree. It is most probable that silica, being exceedingly hard, scratches the surface to which finishes containing it are applied and thus gives a somewhat rough surface to which paints or enamels cling better than to perfectly smooth ones.

#### Asbestine. Talc.

These silicates of magnesium are widely used as fillers and extenders in both the paint and lacquer industries. They are

light, transparent and very cheap, and have the additional advantages of buoying up heavier pigments and thus preventing their rapid settling. They are moderately easy to grind in oils. The color ranges from almost a pure white in the finest talcs to a dirty grey for some samples of asbestos.

Talc is finely ground and sifted soapstone or steatite, the processing of which has become perfected through the wide demand for the substance in the cosmetic industries. The poorer grades are used as fillers. It has a flaky structure and a peculiar soapy feel. The specific gravity is about 2.85.

Asbestine, while chemically very similar, is different in some physical properties. Its structure is fibrous rather than flaky, the material being the short fibers obtained as a by-product in the mining of asbestos. It has the same specific gravity as talc, but a higher oil absorption. It is used far more widely than talc, owing to its much lower price. Traces of iron are occasionally found which may yellow a white enamel.

### BLACK PIGMENTS

#### Bone Black—Ivory Black.

These are very similar pigments, prepared by the dry distillation of bones or ivory waste. They contain only about 15 to 20 per cent of carbon, the rest being inert ash, chiefly calcium phosphate and sulfate. The density is about 2.60. While used in cheap paints, these blacks are not employed to any extent in the lacquer enamel industry, except in tinting where occasionally bone-black in oil is added to attain a certain shade. The artificial leather industry uses large quantities of the material, its cheapness being its chief recommendation. Bone black can be ground more easily than the other forms of carbon and is thus commonly found on the market ground in oil. A variety containing some carbon black to enhance the tinctorial power is called "drop black."

### Lampblack.

By allowing the flame from burning oil to play continuously on a rotating iron cylinder filled with water a heavy deposit of soot is obtained which is scraped off and supplies the lampblack of commerce. This is a soft, powerful black with a density of 1.8. It is the basis of most black paints and enamels with an oil base, where it is ground up with about three times its weight of oil. It is sometimes mixed with small amounts of prussian blue or ultramarine to enhance the black color. Lampblack, as well as carbon black, is very voluminous owing to entrapped air, and as a result it is very difficult to weigh out and handle. It comes on the market in paper bags holding 10 to 12 pounds, packed 12 bags to a case.

Lampblack should contain no grit, as can be determined by rubbing up with a little linseed oil and turpentine. There should be no tarry matter, a test for which consists in pouring a little ether over a few grams of the lampblack on a piece of white paper and noting whether any permanent brownish ring is produced after evaporation of the ether. Its tinctorial power is of importance and can be determined by adding one gram to 100 grams of zinc oxide, grinding up in a mortar with enough turpentine to give a paste, spreading this paste on white bristol board and noting the color in comparison with a definite standard. This method is applicable to all dark colors, and should be used whenever a new lot of pigment is purchased. As standards it is best to keep on hand a pound or two of high-grade pigments of known quality and make the two pastes up at the same time.

### Carbon Black.

This pigment affords the darkest black available, as well as the most expensive. It is greatly favored by the lacquer trade, for a few ounces to a gallon of lacquer gives a flat black of excellent coverage. Carbon black is made by the cracking of natural gas, especially in Louisiana and Texas, and is a very

voluminous, somewhat granular black with a slight brownish cast in dilute suspensions. Its density is approximately that of lampblack. Carbon black, owing to its granular structure, is not as soft or as smooth as lampblack, but has higher coverage and when properly ground up gives a smooth film with pyroxylin that is very durable. A differentiation between lampblack and carbon black can be made by adding the pigment to water. The former floats on water while the latter soon sinks. Carbon black requires four to five times its weight of oil to grind it properly. As before mentioned, it is an expensive pigment, the best grades commanding from 45 to 60 cents a pound, but for high-grade products it is worth the price.

### **Graphite.**

This is really not a black pigment, but a gray one. It is found in nature, particularly in Ceylon, and is also prepared artificially in the electric furnace. The finely pulverized, air floated variety is used to a considerable extent in protective paints, and has a minor use in special lacquers. Graphite has a density of 2.3, conducts the electric current, is inert to most reagents and is very soft.

### **Nigrosine.**

While not a pigment, the extensive use of nigrosine in gloss black lacquers makes it worthy of mention here. Nigrosine is a dye, and is made in two forms, the oil-soluble and the spirit soluble variety. The latter is used to the largest extent by the lacquer trade. Nigrosine is a black dye which in dilute solutions shows a distinct bluish tinge, and which has a high tinctorial power. It is very soluble in alcohols, particularly in wood and ethyl alcohols which dissolve from 10 to 11 pounds of the dye per 100 pounds of alcohol. Nigrosine is generally used in a ten per cent solution in wood alcohol, which is added to the lacquer. Being a dye, and thus transparent, it does not

nullify the gloss given by gums and pyroxylin and is therefore almost a necessity in the preparation of gloss black enamels. Owing to its solubility, films containing nigrosine are prone to bleed if a clear lacquer coat is applied over them.

### BLUE PIGMENTS

**Prussian Blue—Chinese Blue—Bronze Blue—Milori Blue.**

Essentially these pigments are the same, all being ferric ferrocyanides. The difference lies in the process of manufacture. The first step in modern processes is the precipitation of copperas, or ferrous sulfate solutions, with yellow prussiate of soda or sodium ferrocyanide. The resulting white ferrous ferrocyanide is then oxidized to Prussian blue by the action of a mixture of potassium bichromate and sulfuric acid. Bronze blue is made with bleaching powder as an oxidizer and Chinese blue with potassium chlorate and hydrochloric acid. All are blue pigments, with varying casts that make them desirable for different purposes. Chinese blue is considered the best for enamels by many users, although bronze blue gives a unique effect that is sometimes desired. The density of these blues is 1.97.

The ferrocyanide blues are inert to acids, except oxalic and similar organic acids. They are rapidly attacked by alkali, and thus should not be used with whiting or other alkaline pigments or on plaster walls or similar surfaces. Like ultramarine, these blues are somewhat transparent, having poor hiding power despite good tintorial strength and covering power. They are hard, brittle, and rather difficult to grind. The oil absorption is very high.

Good specifications for these pigments require that the material be entirely a ferrocyanide blue with the proper tinting power and fineness of grinding, containing at least 20 per cent nitrogen and 30 per cent iron, less than 1 per cent mois-

ture and less than 1 per cent insoluble in 10 per cent oxalic acid solution.

An excellent pigment, known as Brunswick Blue, consists of 10 to 25 per cent Prussian Blue and the rest blanc fixe. This is a pigment of fine color, easier to grind smoothly than is Prussian blue and much cheaper. It is used to a considerable extent in blue paints and enamels.

### **Ultramarine Blue.**

Formerly a rare and much-prized artist's color made from the expensive mineral lapis-lazuli, ultramarine is now the commonest and widest used blue pigment. This is due to its manufacture from cheap and abundant materials, a process invented by Gmelin in 1828. By his method sodium carbonate, kaolin, charcoal and sulfur are heated together to a green mass, which is subsequently heated with more sulfur and then gives the commercial ultramarines. The colors of the resulting pigment varies from green to reddish violet, depending on the time and temperature of heating. Another process now used starts with sodium sulfate instead of the carbonate. The first is called the soda process, the second the sulfate process. Good products can be made by either method, but the second is apparently more economical, and of a darker, more opaque hue.

Ultramarine has the approximate composition of 4 molecules of sodium aluminium silicate, one of sodium sulfide, and one of sulfur. The color is apparently due to a colloidal dispersion of some solid, probably sulfur, in the mass. It is this sulfide and sulfur content that renders it unwise to use ultramarine with pigments containing copper, lead or zinc, for the sulfides of these metals are black and thus spoil the original color. Ultramarine pigments are resistent to alkali, but rather easily affected by acids. It should be tested for tinting power by adding one part to 50 of zinc oxide in clear lacquer or pale oil and comparing the resulting tint with that given

by a standard blue under the same conditions. Since its composition is variable, a chemical analysis is generally of little value, but determinations of moisture and fineness should be made. For lacquer use a product that passes completely through a 300-mesh sieve is required, and an even finer grinding would be preferable. The density of an average ultramarine is 2.50, giving a bulking value of 20.85 pounds to the gallon.

A product made by the action of ammonium chloride on ultramarine is known as cobalt blue (a poorly chosen name as it is confused with the true blue made from cobalt) and owing to its fine, bright, light-blue color has found a growing demand.

### **RED PIGMENTS**

#### **Oxide Reds—Turkey, Indian, Venetian Reds.**

By heating copperas, an iron sulfate obtained in large quantities as a by-product of the pickling of iron and steel, an oxide of iron is produced of wide utility as a red pigment. This ferric oxide is of the same composition as rouge, has remarkable permanence, excellent hiding power and is quite cheap. Turkey or Indian red is quite a pure product, averaging 90 to 95 per cent of ferric oxide, and having a density of 5.12 to 5.30. Venetian red is prepared by heating copperas with limestone and is a mixture of iron oxide and calcium sulfate averaging from 25 to 40 per cent ferric oxide. For use in lacquer enamels it seems most advisable to buy the higher concentrations of Indian or turkey red. These come in various shades, from yellowish red to a purplish red, and often afford the most economical way to obtain certain desired colors. The purplish red oxide, for instance, will replace an ultramarine-para-toner mixture costing considerable more. For the bright scarlets and reds, however, these pigments are too dull and have been replaced in great measure by the red lake pigments.

Tuscan red is a combination of the two, consisting of a mixture of venetian red and an alizarin-lake.

Oxide reds are liable to contain either free acid or alkali, and should be tested by shaking up 5 grams with 100 c.c. of water, allowing to settle, and testing the clear liquid with blue and red litmus paper. No change in color should be observed.

An advantage of these reds in tinting up whites to pink, flesh, tan, etc., is that they do not bleed, or dissolve in the solvents used, as the lake red do. This is of importance where the enamel coat is to be treated with a finishing lacquer, for a bleeding red will tend to spoil the effect.

One of the important uses of red oxides is in the manufacture of the so-called oxide primers. These are composed of red oxide, varnish oils such as tung or linseed, dryers, and thinners such as turpentine or petroleum spirits. The experience of the automobile painter thus far has been that the best results are obtained by using such a primer on the metal and then bringing up the finish upon this as a base with pyroxylin surfacers and enamels. The function of the red oxide is to protect the metal against rust, against which the iron oxides have been found to be of the highest value, and also to give a color to the primer which will show whether or not the surface has been completely primed.

These primers are so compounded that they dry hard enough to permit of the application of lacquer in 18-24 hours, if the primer is allowed to dry in the air; while automobile factories provided with baking facilities can force-dry the material in a few hours.

It may be that a lacquer primer that is durably tenacious and waterproof will be developed, and for many purposes the present products are satisfactory, but for the very highest quality of finish on metal the use of an oil primer seems at present the best and safest procedure.

### Toners and Lakes.

Toners are organic dyes which because of their permanence and tinting strength have been found suitable as pigments. Lakes are combinations of these dyes with inert mineral carriers, such as alumina or blanc fixe, generally obtained by forming the dye in the presence of a pulp of the extender on which it is firmly absorbed.

For red enamels the paranitraniline red lake, the so-called para toner, and the para toluidine red have achieved most prominence. Both the pure dyes and the let-down lakes are used.

### Para Toner—Paranitraniline Red.

This dye is formed by diazotizing paranitraniline and coupling it with beta-naphthol or beta-naphthol R. The dye can be adsorbed on barytes and after washing, drying and pulverizing, a bluish red powder results containing 10 to 20 per cent of the dye and 80 to 90 per cent barytes. Para red is fairly permanent to light, has fair opacity and great tinctorial value. It has a marked tendency to bleed in the presence of ordinary lacquer solvents. The enamels made with para red have a slightly bluish cast and when mixed with such pigments as chrome yellow it is observed that instead of a pure orange a slightly brownish one is produced. Para toner is sold in the concentrated form, or extended with barytes or other fillers.

### Lithol Red.

2-naphthylamine sulfonic acid is diatonized and coupled with beta-naphthol in the presence of blanc fixe to produce lithol red. This lake generally contains from 5 to 10 per cent of dye, although the concentrated pigment is also to be had. Lithol red has also a bluish cast, but is a somewhat purer red

than para toner. It is asserted to be non-bleeding, but certainly not all of it is, as lacquer solvents extract appreciable amounts of color. A good test for bleeding is to grind up some pigment with a little 8-ounce pyroxylin solution, allow it to dry and then spray a white enamel over it. Any bleeding will be evidenced by a pinkish tinge imparted to the white.

### Toluidine Red—Helio Fast Red.

This is the best and most expensive red pigment. It is made by diazotizing meta-nitro-para-toluidine and coupling it with beta-naphthol, sometimes striking the lake on blanc fixe and sometimes on aluminium hydroxide. It contains 10 to 20 per cent of the dye, is more permanent than either of the other lakes, has a higher tinting power and better coverage, has a much less pronounced tendency to bleed and will stand a higher temperature than any of the others. Like Para and Lithol Reds the pure dye or toner can be bought and is often used in lacquers.

Moreover its color is a yellowish or scarlet red. Toluidine red is the standard for many railroads, oil companies and other industries requiring a red enamel that will stand exposure. Its price is high, but it can be extended considerably with cheap fillers and thus the price is brought down to a practical point.

Lakes of certain orange, maroon, burgundy and similar hues are often used, as these colors cannot be satisfactorily duplicate by mixtures of pigments.

The density of these lakes is practically that of the material on which the dyes are adsorbed, 4.46 for barytes, 4.28 for blanc fixe, or 3.75 to 4.0 for alumina. The dyes themselves have a density of about 1.4 to 1.6. The pure dye toners are often used, and contain practically no extender.

### BROWN PIGMENTS

#### Umber.

Umber is an earth pigment, similar to ochre, but containing manganese as well as iron. The best variety comes from Cyprus, and is called Turkey umber. The raw umber has a brown color with a greenish undertone. It is used to a considerable extent in the making of stainers and grainers for wood-working. For most paints and enamels the burnt umber, which is made by careful heating of the raw material, is preferred. This has a rich reddish brown color, is slightly more transparent than the raw umber, and like it is very permanent both to exposure and to admixture with other pigments. Umber grinds easily to a smooth paste and gives an excellent brown enamel. It can be used to make buffs, olive greens and other colors where it replaces more expensive pigments.

Burnt umber has a density of about 3.75 and contains 40–55 per cent ferric oxide. It is tested by adding one gram to ten grams of zinc oxide and comparing the resulting tint with that produced by a standard umber.

Browns of various shades can be made by mixing green and red, with black or white to lighten or darken the color.

### YELLOW PIGMENTS

#### Ochre.

Ochre is a clay containing yellow oxide of iron in sufficient quantity to make it usable as a pigment. The best ochre is that imported from France and is known as French ochre J.L.C.E.S. Other grades with similar combinations of letters, which serve as a shorthand abbreviation of the source, quality and color, are on the market. For many purposes the cheaper American ochres are equally good and are worthy of trial. Specifications should demand at least 20 per cent iron calcu-

lated as ferric oxide and less than 5 per cent of lime, none of which should be uncombined. The material should be bone dry and not agglomerated into lumps.

Ochre is a very valuable pigment, due to its permanence, cheapness and ready grinding in oil. It is somewhat transparent, and for use in lacquer enamels is often sold tinted up with 10 per cent chrome yellow, which increases the opacity markedly. Many painters insist on an ochre priming coat on wood. An important test for ochre is that for grinding power, and this can only be done properly by grinding a sample batch in a small pebble or similar mill and testing out the resulting enamel. This is advisable owing to the fact that admixture of grit or hard, slow grinding particles of ochre itself is not uncommon.

The density of ochre is 2.8 to 3.2 and its bulking value about 25 pounds to a gallon.

An artificial yellow oxide or iron, called "ferrite yellow," is rapidly replacing the natural ochre in lacquers. This material has the color of ochre but much greater tinting and hiding power, so that its use is an actual economy.

### Chrome Yellows.

A variety of yellow pigments of great merit can be made by the reaction between solutions of lead nitrate or acetate and of potassium bichromate. The very light shades are made by keeping the solutions very dilute, about 2 per cent, using alum, and carrying on the reaction in the cold. By washing the precipitate, filter pressing and drying at low temperatures the light primrose or lemon yellow chromes are produced. These are mixtures of lead chromate and sulfate, and do not have the opacity of the darker yellows containing more of the lead chromate.

The medium chrome yellows are the ones generally used in making enamels. The solutions used are more concentrated, less alum is used, and the reaction is carried on at about

200° F. By boiling the solutions a pale orange chrome can be obtained.

The medium chrome is a pigment of high opacity and tinting strength. It is reddened by alkalis and darkened by sulfur fumes. The chromate dissolves in dilute nitric acid, while the sulfate does not, and this affords a simple means for determining the ratio of these components. The more chromate the better the opacity.

Chrome yellow is very heavy, having a density of 5.89 to 6.7. It should contain less than 1 per cent of water, at least 98 per cent of lead salts, and when mixed with Chinese blue should give a pure green of equal depth to one made with a standard chrome yellow. When added to 10 times its weight of zinc oxide in linseed oil it should give a tint of satisfactory color.

As it contains lead, it should not be used with lithopone, ultramarine or other sulfur-containing pigments, since the sulfur is liable to blacken it.

By treating with alkali, an excellent orange pigment, chrome orange, is produced.

### Cadmium Yellow.

This is a cadmium sulfide, an excellent pigment in every way but too expensive for any ordinary use. It is used for artists' paints, and may be of value in a lacquer enamel of the highest grade, if the particular shade of yellow is desired.

### Dutch Pink.

Despite the name, this is a yellow color made by adsorbing quercitron, a natural yellow dye, on barytes or alumina. It is fugitive in the light but is used somewhat because of its yellow tint being observable under artificial light. It is of very minor importance in lacquer enamels. It has a specific gravity of about 2.5.

### ZINC CHROMATE

The chromate of zinc is finding a vogue in lacquers, as its pure tone and light weight make it preferable to lead chromate in delicate greens, ivories, etc. It does not separate from other pigments as readily as the lead yellows, and this is quite an advantage in automobile enamels. Moreover it is not darkened by sulfur fumes. While non-bleeding in organic solvents, it does bleed in water and especially so in alkaline solutions.

### GREEN PIGMENTS

Since the number of shades of green made and sold is almost unlimited, many makers use ultramarine, prussian blue, ochre and chrome yellow to make up their greens. These mixed greens, however, do not give the pure colors sometimes desired and green pigments are used to some extent.

#### Chrome Green.

Chrome green is made by mixing a pulp of chrome yellow and water with a similar pulp of barytes or blanc fixe, stirring in a pulp of chinese blue, mixing thoroughly, washing, filter-pressing and drying. The dry powder is ground in edge runners and sifted to 80- or 100-mesh fineness. The green thus obtained is quite different from one made by merely mixing the chrome yellow and blue, and is a much better product. It has good covering power, but is acted on by acids, alkalis and sulfur. The density depends on the proportions taken, but is generally about that of baryta.

C. P. chrome green is made by precipitating lead chromate upon prussian blue, no extender being used.

The specific gravity varies from 3.5 to 5.3 for the C. P. colors depending on the shade.

**Chromium Oxide Green—Guignet's Green.**

This is the most permanent of all greens. Unfortunately it is rather expensive and of low tintorial power and is thus only used in the better grades of enamels. It is made by heating potassium chromate with boric acid, thus obtaining a chromium borate, which is then decomposed by steam to give a hydrated oxide of chromium which is the very excellent chromium oxide or Guignet green. The color given by this pigment cannot easily be duplicated by mixtures of other pigments and it is well to be able to supply it if required. It is very permanent to light and heat, and of increasing importance in automobile enamels. Its specific gravity is about 5.0.

**Verde Antique—Copper Carbonate.**

Copper carbonate, made by precipitating blue vitriol with sodium carbonate is used to a slight extent in lacquer finishes to give the old brass and copper effect. It has too little coverage and opacity to be of much use otherwise.

**BRONZE POWDERS**

These may be classified as pigments composed of metallic alloys in a fine state of subdivision, and are used in enormous quantities in conjunction with pyroxylin bronzing liquids. The bronzes come in a wide variety of colors, depending on the nature of the original alloy and on the treatment.

Pure copper is melted in an oil-burning, brass-melting furnace and pure zinc is added to give the desired alloy.

Rich gold....	Copper 80 per cent, Zinc 20 per cent
Rich pale gold	Copper 85 per cent, Zinc 15 per cent
Pale gold....	Copper 90 per cent, Zinc 10 per cent
Red gold ....	Copper 95 per cent, Zinc 5 per cent

Other alloys are used for special shades. The liquid alloy is then poured through a machine that makes pieces about the

size of a silver dollar. These are then run through hammer machines, which beat them to a thin sheet and break the sheet up into pieces about the size of a quarter. These are screened and the oversized pieces returned to the first machines. The rest go to a second set of hammers, which are lighter than the first, and beaten there for 2 hours to 5-mesh size. A flitter machine then reduces these to 20-mesh size, or flitter, which is then given a final hammering to the desired powder, or really very fine flakes. Eight hours of hammering will produce a powder of 120-mesh fineness, while the 200-mesh size requires 14 to 24 hours to produce.

After hammering and grading, the powders are polished in a steel drum with revolving brushes. Stearine is used in the polishing.

Cheaper grades are made by using scrap zinc and copper, but the best quality is obtained by using pure metals.

Aluminum powder is also widely used.

#### **GENERAL DISCUSSION OF PIGMENTS**

The qualities most often demanded of any pigment are fineness, opacity, tinting strength, permanence, brightness or luminosity. Rate of settling, apparent volume, specific gravity and uniformity of color are usually determined, while in very large organizations buying in carload and larger lots a chemical analysis of the pigment is usually made.

For use in enamels pigments should be very finely ground, generally 300 to 350 mesh. A set of sieves 3 inches in diameter with a bottom pan that fits snugly are generally used for determining fineness. The usual sieves for this work are the 100, 200, 250, 300, 325-350 mesh. Ten grams of pigment are placed in the sieve of finest mesh, a dozen or so steel balls added, and the sieve shaken to and fro till all the fine particles have settled into the bottom pan, which, of course, has been previously weighed. The increase in weight, represents the amount passing through the sieve. The residue is then brushed

into the next finest sieve and the process repeated. For lacquer enamel work there should be no particles larger than 250 mesh and less than one per cent larger than 300 mesh. A weighted scale for fineness has been proposed that merits description. By starting with a ten-gram sample and multiplying the amount passing through a sieve by the mesh of the sieve adding, and multiplying by a factor depending on the mesh chosen as standard, the fineness can be expressed directly as percentage. For instance, let us assume that we choose the 250 mesh as standard. Seven grams pass through this sieve, 1.5 grams through the 200-mesh, 1 through the 150- and 0.5 through the 100-mesh sieve.

$$\begin{array}{rcl} 7 \times 250 & = & 1750 \\ 1.5 \times 200 & = & 300 \\ 1 \times 150 & = & 150 \\ 0.5 \times 100 & = & 50 \end{array}$$

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$$2250 \times 0.04 = 90 \text{ per cent fineness}$$

If we had chosen the 200 mesh as the standard we would have had  $2250 \times 0.05$  or 112.5 per cent. Any loss in the sifting is accredited to the average of the meshes used. Of course this system in itself is not an infallible guide, as some very fine and some very coarse material might give a good average but yet not be very suitable for grinding. By imposing a condition that there should be no material below a certain minimum fineness this is obviated.

#### Rate of Settling.

This property of pigments is of considerable importance in all paint and enamel manufacture. Any suspended solid particle has a definite tendency due to the force of gravity to settle at the bottom of the container. This tendency is dependent on the viscosity of the vehicle, on the specific gravity of both vehicle and pigment, on the size of the pigment particles. Coarse particles settle faster than fine ones, and heavier par-

ticles faster than light ones: consequently, some estimate of the settling propensities of the pigment can be made by noting the time required for a definite amount of the pigment to settle a definite distance in a standard medium. To save time a medium of very low viscosity, such as 87° or 72° gasoline is used. The simplest method is to sift some of the pigment through a 150- or 200-mesh sieve, take 5 g. of the powder and place it in a graduated 100-c.c. cylinder, add a little of the benzine or gasoline and stir with a fine wire till all the air bubbles are out, then fill to the 100-c.c. mark with the liquid. The volume of the pigment is noted, the cylinder covered by the palm of the hand and shaken 25 times, then allowed to settle and the time required to reach the original volume recorded by a stop-watch. A more accurate modification is the Stormer method, wherein 2 grams are shaken with 50 c.c. of liquid as before and the time required to settle to the 25-c.c. mark noted. This is made more accurate by using a metal shield with a hole exactly opposite the 25-c.c. mark and an electric light bulb in line with the hole and the cylinder. By looking through the cylinder the moment when the pigment settles below the mark can be noted when the bulb filament becomes visible.

Settling can be overcome in part by the use of certain light, buoyant pigments, such as china clay and asbestos, which seem to exert a definite help in maintaining heavier pigments in suspension.

### Opacity.

By opacity or hiding power is meant the power of obscuring the surface to which the paint or enamel is applied. It depends on the chemical composition of the pigment, on the amount present in the enamel, on the structure of the pigment and on the difference in refractive index between the vehicle and the pigment. Generally speaking amorphous pigments are more opaque than crystalline ones, but the so-called crypto-

crystalline condition wherein the exceedingly minute crystals are connected with an amorphous matrix seems to give the maximum opacity. The titanium whites, for instance, belong to the crypto-crystalline type. Some pigments that are opaque in oil are transparent in water, and vice versa.

The best test for opacity of a pigment is to grind it up with oil or lacquer in definite ratio and apply it to a porcelain plate with black parallel lines, and comparing the result with a standard pigment treated similarly. Since white pigments are the ones in which opacity is of most importance, a quick estimate can be made by adding some standard prussian blue or chrome yellow pigment to 25 and 50 times its weight of the unknown pigment and noting the shade produced in comparison with a standard white of the same chemical nature. The more transparent the white, the darker will be the shade produced. The Pfund cryptometer, U. S. P. 1,468,075, is a more scientific and accurate measure of opacity.

Opacity is sometimes incorrectly called covering power. The latter term should be restricted to the property of a pigment which governs its covering a surface, regardless of whether it hides the surface or not. Covering power depends on the chemical nature of the pigment and on its fineness. For equal fineness the coverage is inversely proportional to the specific gravity of the pigment.

#### Specific Gravity of Pigments—Bulking Value.

The simplest method for determining the specific gravity of a pigment is to weigh out 10 to 15 grams, add it to 80 c.c. of benzine, water or other liquid of known specific gravity and observing the increase in volume after the air bubbles have been disentangled from the pigment by a fine wire. If water is used, the weight of pigment divided by the increase in volume gives the specific gravity directly. Some pigments are only with difficulty wetted by water and other liquids have to be used, such as benzol, gasoline, etc.

For greater accuracy the specific gravity bottle or pycnometer is used. This is a glass bottle holding 50 c.c. and provided with a ground glass stopper containing a thermometer. A capillary side-arm is fused into the bottle near the neck and is bent vertically at right angles. The bottle is weighed ( $W$ ) and filled with a liquid, generally at  $20^{\circ}$ , by adding liquid till the bottle is full, then inserting the thermometer and stopper so as to force the excess out of the capillary side-arm, which is then closed with a ground glass cap to prevent evaporation. The bottle is again weighed ( $W'$ ). A bottle is standardized by filling with water at known temperature and then determining the volume as follows.  $\frac{W' - W}{d} = V$ , where  $d$  is the density of water at the temperature taken. Let us assume that its volume is exactly 50 c.c. Now repeating the process using benzine we find that the weight of the benzine is 40 grams, its volume is 50 c.c. and the specific gravity of the liquid is thus 0.800.

The pycnometer is cleaned out, dried and about 2 to 5 grams of pigment weighed into it. It is then filled with benzine, care being taken that no air bubbles are left. A second weighing gives let us say 43.252 grams, for 5 grams pigment. There are thus  $43.252 - 5 = 38.252$  grams of benzine in the bottle, corresponding to 47.815 c.c. The volume of pigment is then  $50 - 47.815 = 2.185$  c.c. and the specific gravity is  $\frac{5}{2.185}$  or 2.29.

The bulking values of pigments are found from their specific gravities by multiplying them by the weight of a gallon of water or 8.337 lbs. This gives the weight of the pigment in pounds per solid gallon, i.e., a gallon containing no air spaces. The pigment above illustrated, for instance, would bulk  $2.29 \times 8.337$  or 19.09 pounds to a gallon. Strictly speaking, the water bulking value obtained above is slightly inaccurate for pigments ground in oil or lacquer, inasmuch as the weights per gallon of these vehicles is less than that of water. How-

ever, many paint makers maintain that the use of the water bulking value gives them better results than the strictly accurate oil value.

[N. B.—A very complete account of the determination of specific gravity, together with exhaustive data on pigments, is found in Circular 148 of the Paint Manufacturers Association.]

### Tinting Power.

The coloring or tinting power of a pigment is best determined by adding a known weight to 25 or 50 times its weight of zinc oxide ground in poppy seed oil, dammar varnish, etc., and comparing the tint with one obtained from a standard pigment of the same chemical nature treated similarly. The Lovibond tintometer affords a useful means of matching colors, but a very close approximation can be obtained by a practiced eye. It is well to use at least two proportions of zinc oxide and unknown pigment if the latter is of intense coloring power, for it often happens that a standard and an unknown will match closely at 1 part of pigment to 25 parts of white, while at 1 to 50 dilution the standard is markedly different.

Luminosity, trueness to shade, and many other properties of the pigment reveal themselves to the skilled eye after grinding up small portions with oil or lacquer and comparing against standards. For most purposes such a qualitative examination is more important than a chemical analysis, which may entail untold labor and give meaningless results.

### Permanence toward Light.

A simple apparatus devised by Dr. H. A. Gardner serves very well to test out the permanence of pigments as well as finished enamels toward light. It consists of a two-compartment box, one part being painted black and the other white and containing a shallow pan for water. A 75-watt blue glass Mazda light is placed in the white compartment. By applying

the enamel, or a grind of the pigment and oil, to two pieces of metal or wood, placing one in the black compartment and one in the white illuminated one, an opinion as to the stability toward light can quickly be reached. The conditions of intense illumination, high temperature and high humidity obtained in this apparatus are very severe, and are sometimes accentuated by the substitution of a quartz ultra-violet light for the daylight bulb, and by the use of ammonia in the water.

Stability to sulfur and similar fumes can be tested in such a cabinet by the use of ammonium sulfide solution or by passing the vapors of sulfur dioxide, ammonia or hydrogen sulfide through the box.

The microscope in practiced hands can give much information as to the constituents of a pigment, approximate size of particles, etc., but it is seldom required if other tests are satisfactory. After all, the real test of a pigment is not what it is, but what it does.

### **Oil Absorption.**

It was early learned by paint grinders that pigments varied greatly in the proportion of oil required to grind them to a stiff paste. This variation was in general a specific characteristic of the pigment taken, and even those of identical chemical composition, e.g., barytes and blanc fixe, varied greatly in their oil absorption values. Knowledge of a pigment's capacity to take up oil is, of course, quite important to paint grinders and tables of oil absorptions are to be found in many books on the subject such as Smith's "Manufacture of Paint." These values are given for linseed oil, in which practically all paints are ground, and are not accurate for castor oil, the medium used most frequently in the pyroxylin industries. Through the courtesy of Mr. Weidig and Mr. Eriksen of the Keratol Company the writer is able to give the following table of oil absorptions in Baker's AA castor oil. The method of determination was that used by Gardner and Coleman (Cir-

cular 85, Paint Manufacturers' Research Institute) and the values given are the grams of castor oil required to cause 100 grams of pigment to "ball." Some of Gardner and Coleman's values are also listed to show the variation between linseed and castor oils.

Pigment	Oil Absorption in Castor oil (Erikson)	Oil Absorption in Linseed oil (Gardner)
Zinc Oxide	25.5	52
Lithopone	26.9	33
Asbestine	35.5	50
Whiting	24.0	32
Titanox	21.2	
Chrome Yellow (primrose)	26.9	
(medium)	21.1	
Chrome Orange	11.1	
Chrome Green C. P. (medium)	45.6	
(dark)	61.0	
Chrome Oxide Green	15.4	
Ultramarine Blue	32.6	
Prussian Blue	91.6	
Toluidine Red (20%)	49.4	
Ground Slate	33.8	
Bone Black	50.—60	
Ochre	39.4	
Umber (Burnt)	57.6	
Red Oxide C. P. (light)	42.7	
(dark)	18.0	

It generally requires 10 to 15 per cent more oil than the above to grind the pigments properly in 3-roll or similar mills. For use in pyroxylin enamels, pigments of very low oil absorption are to be preferred.

## PART TWO

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### CHAPTER VIII

#### BRONZING LIQUIDS AND LEATHER DOPES

With the pyroxylin, resins, solvents, plasticisers, etc., that have been described in Part One an infinity of formulae can be built up. The simplest solutions are those containing pyroxylin alone, and many of the standard bronzing liquids and leather dopes belong to this class.

The first step in making any pyroxylin product is the dissolving of the pyroxylin. This, on the large scale, is not as simple as dissolving salt in water by any means. The fibrous nitro-cellulose is only slowly attacked by solvents, and when the outer portion of a lump has been gelatinized by the solvent the inner layers are very hard to dissolve. For this purpose energetic agitation is required, generally coupled with a shearing or tearing action of blades or points in the agitator or mixer. A good piece of apparatus should have a large man-hole for the introduction of the bulky pyroxylin, and a gate valve for drawing off the solution if made too heavy to pump. In large installations pipe fittings for using an air lift to transport the pyroxylin to the clarifiers, filter presses or centrifuges should be provided. Naturally, since the solvents are very volatile the apparatus should be practically air tight. A form often used consists of a horizontal steel drum of the required capacity, provided with manhole, draw off valve,

vent, etc., and with a horizontal shaft running through well-packed stuffing boxes and provided with a number of sharp-edged blades set at an angle. The lining should be of tin or white metal, and the shaft and blades of monel or similar non-corroding material. Otherwise traces of iron or copper may go into solution and cause discoloration. An advantage that is often overlooked is the use of a jacket through which steam or water can be run. This permits of controlling the viscosity of the solution to some extent and to control the heating up of the solution due to the heat of solution of pyroxylin.

Another type of apparatus is the revolving churn as illustrated in Fig. 1. This is studded inside with sharp points that break up the resin or pyroxylin particles and permit of easier solution. They are made in 50-gallon to 200-gallon capacity, and since they are excellent for dissolving resins and scrap celluloid or picture-film have a place in any completely equipped lacquer establishment. Where larger volumes are to be handled at one time, or whenever fibrous pyroxylin is used, the first mentioned apparatus is more suitable and can be designed and built to suit the necessities of the plant.

Fig. 3 represents another widely used type of dissolver.

In this connection it may be remarked that many of the smaller lacquer makers do not cut or dissolve their own pyroxylin, but buy it from the large makers already dissolved in any formula they may choose to specify. The common basis is a 16-ounce or 32-ounce solution of the required viscosity, acid-free, free from specks or dirt, light in color and packed in 50- or 100-gallon drums. The thick pastes are sold in open-head steel barrels. The basis for the price charged by the makers of these solutions is the market price of the solvent mixture plus the market price of the pyroxylin, their profit coming in the expansion of the solution and occasionally in bargains in the materials due to their large purchases. The small lacquer manufacturer buys these solutions, mixes them with gums, oils, thinners, etc., and sells the finished product. He is thus enabled to do without the expense and fire hazard

of making his own solutions and clarifying them, but of course does not make the 10 or 20 per cent profit on the expansion.

In making pyroxylin solutions, some manufacturers add the solvent mixture directly to the nitrocellulose. Others add the non-solvents, the alcohols and hydrocarbons first and grind the pyroxylin with it so as to have the liquid penetrate all the pores. The solvent is added next, and apparently acts more energetically on the material than in the first procedure. It

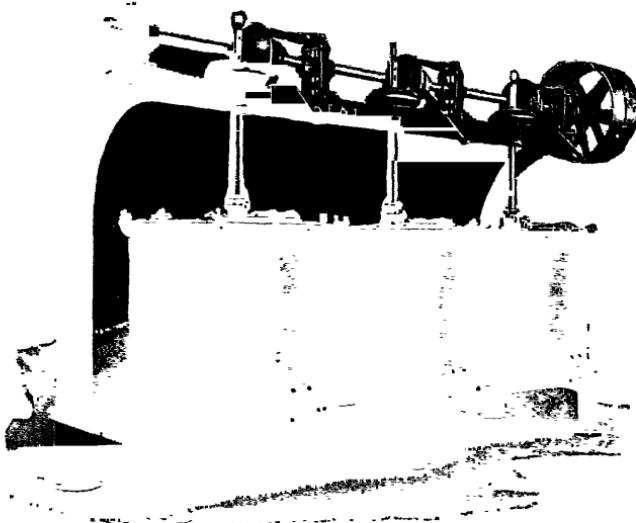


FIG. 3.—Pyroxylin dissolving and mixing tanks.

takes at least 8 hours to get a satisfactory solution of the higher concentrations and viscosities.

#### Clarification.

Pyroxylin solutions generally contain some undissolved material, either unnitrated cotton or too highly nitrated cotton that is not soluble in the liquid. They must be clarified for use as clear metal or wood lacquers, although for cheap enamels or leather dopes this is sometimes dispensed with. In fine

enamels it is found that the fiber particles are stiffened by pyroxylin on drying and thus make the enamel rough.

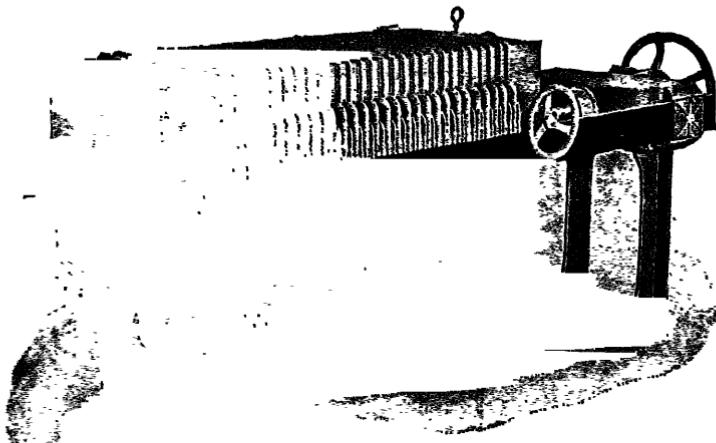
The oldest and simplest method of clarification consists in allowing the material to settle for several days or longer in large settling tanks, generally with the addition of barytes, kieselguhr or similar flocculating agent which carry down the fine particles with them. The clear liquid is drawn off through faucets at various levels and the residual sludge used in the very cheapest types of pyroxylin fillers. The solutions thus obtained are not of maximum clarity, and there is considerable tying up of capital and fire-risk involved.

The filter press of the Sperry or Shriver type is often used. Since the material may be of high viscosity, pressures of 80 pounds to the square inch or higher may be required to force them through the filters. For the initial cost, the filter press is probably the cheapest and most efficient clarifier, but it is being rapidly displaced by centrifugal clarifiers of the de Laval or Sharples type. The filter press is troublesome to operate and clean, there is considerable material lost on the papers, and the very finest haze seems not to be removable by filtration alone. Fig. 4.

The centrifuge is essentially a moving bowl, rotating at great speed, in which components of a solution which differ in specific gravity are separated by an enormously increased gravitational force. In the Sharples Super-centrifuge the force exerted is 16,000 times that of gravity with a consequent rapid clarification. The Sharples centrifuge uses a cylindrical bowl, geared and shafted to be rotatable at enormous speeds (up to 15,000 R.P.M. and a peripheral speed of about 6 miles a minute). The bowl is 30 inches long and  $4\frac{1}{2}$  inches outside diameter. The liquid to be clarified is fed into the bottom of the bowl, where by the rapid rotation the solids are carried to the outside of the liquid stream and the clarified liquid continuously emerges from the top, the solids accumulating in the bowl and being periodically cleaned out. The capacity varies from 200 gallons of thin liquid per hour per unit to 20 gallons .

of viscous material per hour. The manufacturers claim an operating cost of about 60c per hour. Fig. 5.

A type of cloudy haze often found in pyroxylin solutions does not seem to be separable even at the highest speeds of the centrifuge, and requires such a device as the de Laval filter centrifuge for its removal. Here centrifugal force is combined with a system of corrugated plates and filter papers so arranged that the rotating centrifuge, after separating the gross



T. SHRIVER & CO.  
Harrison, N. J.

FIG. 4.—Filter press.

particles from the liquid, forces the latter through the filter paper and thus secures the combined effects of gravity settling and filter-pressing with an advantage in time required over both of them. The de Laval centrifuge differs from the Sharples in the shape of its bowl, which is more hemispherical than cylindrical, in the speed of rotation (about 6000 R.P.M.) and in the method of feeding. Here the solution is fed in through the top of the bowl and goes to an inner chamber where the heavier particles are thrown out. Thence it passes to the outer chamber where the finer solids are removed and

the clarified liquid is next forced upward to the discharge tube.  
Fig. 6.

As motive power for centrifuges, belt driving is giving way to electric or steam-turbine driving.

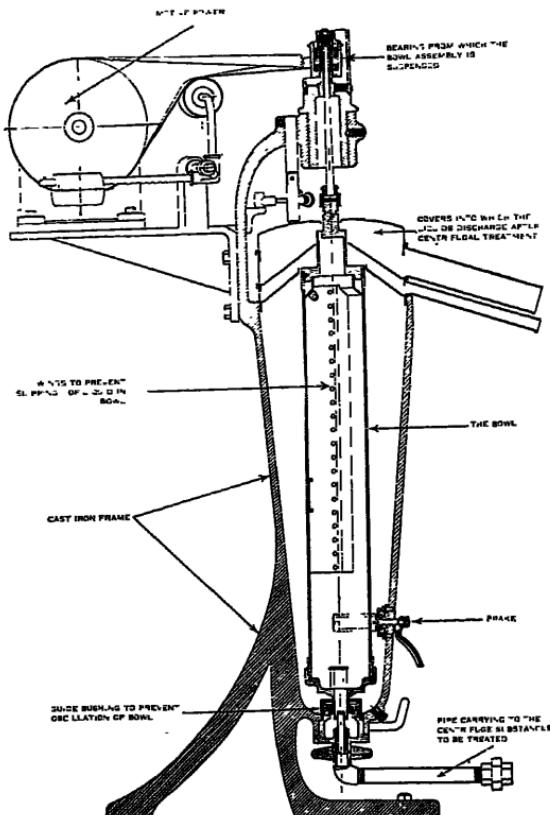


FIG. 5.—Centrifuge.

### Bronzing Liquids.

Assuming that we have available clear solutions of cotton as a stock from which bronzing liquids are to be made, the determining of the formula is influenced by many considerations. The purpose of these liquids is to act as a conveyor for the aluminum or copper-zinc powders used in great quantity as ornamental finish for chandeliers, picture frames, furniture,

metal boxes, etc. Since the business is very competitive, economy of formula is essential. Free acid is very detrimental to the copper bronzes, causing them to turn green and gelatinize. A high viscosity is almost invariable, first because the users are accustomed to this thick material and secondly because the bronze stays better in suspension. Extra body is generally supplied by cheap resins, such as ester gum.

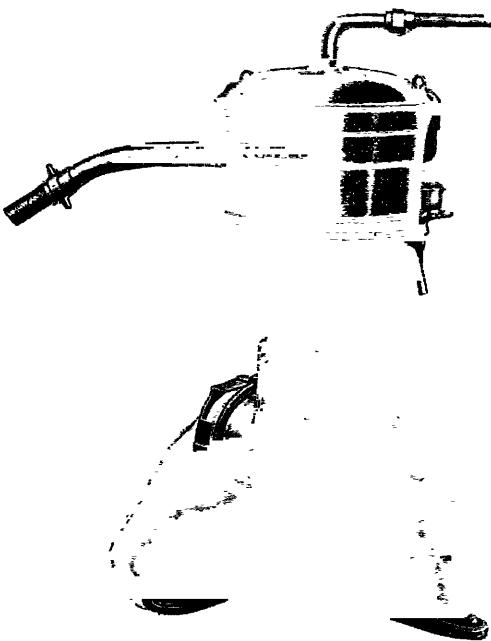


FIG. 6.—Centrifuge.

Bronzing liquids are made in three main classifications according to the quality of solvent. The highest grade will not blush under any normal conditions even in summer humidity. This is a high priced article and wasteful for use in most weather where a much cheaper product will serve the purpose. Some makers of high grade metal or wood specialties use it because they believe that the trouble of having several grades

of bronzing liquid and changing to and from them, together with the risk of spoiling some of their finished goods counter-balances the decreased cost of materials.

The medium grade will work for the greater part of the year, but will blush under extreme conditions. This can be gotten around by using a fortifier or retarder, a high-boiling solvent such as amyl acetate or butyl propionate which is added to the solution on exceptionally humid days.

The lowest grade of bronzing liquid, and the one most widely used, is composed of cheap low-boiling solvents almost entirely, will blush in any humid weather and is used to a very large extent by the lighting-fixture trade who sometimes use fortifier with it and sometimes simply do not spray in the bad weather.

They all contain from 4 to 8 ounces of high viscosity pyroxylin per gallon with occasionally some resin or castor oil to give more body and gloss as well as flexibility which is required by such objects as chandelier chains.

With all pyroxylin products are sold "thinners" or diluents, generally of the same composition as the solvent mixture in the lacquer. Sometimes, for competitive purposes, the quality of the solvent in the lacquer is lowered and that of the thinner raised, but it is obvious that no particular end can be gained thereby beyond the fact that the salesman can claim that his lacquer is lower-priced than the next man's. The upshot is that often the buyer uses one man's lacquer and another's thinner with results that lead often to complaints.

The bronze powder in a low-bodied lacquer is often partially on the surface of the film and thus exposed to the action of the air, moisture and fumes. For this reason it is generally covered with another coat of pyroxylin which serves to protect it. The manufacturers of the cheaper goods use the same bronzing liquid as a top coat, but a real metal lacquer gives better results.

A peculiarity of bronze powders is their habit of gelatinizing pyroxylin solutions. For this reason they are generally

mixed with the liquid in proportions of 1 to 5 pounds per gallon just before application.

The number of formulae is legion, but the following will serve to display the general types.

#### High Grade Bronzing Liquid

8 oz. pyroxylin (dry weight)
1 qt. butyl acetate
1 pt. amyl acetate
1 pt. butanol
1½ qts. toluol
½ oz. castor oil

#### Medium Bronzing Liquid

8 oz. pyroxylin
1 qt. ethyl acetate
1 pt. butyl acetate
1 pt. denatured alcohol
1 qt. benzol
1 qt. toluol.

#### Cheap Bronzing Liquid

6 oz. pyroxylin
2 pts. ethyl acetate
1 pt. methyl acetone
¼ pt. butyl acetate
1 pt. denatured alcohol
2½ pts. benzol
1 pt. toluol
2 oz. ester gum solution.

#### Flexible Bronzing Liquid

6 oz. pyroxylin
2 pts. ethyl acetate
1 pt. methyl acetone
½ pt. butanol
3 pts. benzol
1½ pts. toluol
½ pt. elemi solution
¼ oz. castor oil

The pyroxylin used in these formulae should be of the high viscosity type, 40 seconds or higher and free from acid. The elemi and ester gum should be dissolved previously as described under resins. Unless otherwise specified, 6-lb. cuts of resins are used in these formulae. The general procedure is to start with a pyroxylin solution of 16-oz. concentration in the solvents used, and adding the gum solutions and oil to the solution after thinning to the requisite pyroxylin content with the same solvent mixture. As fortifiers amyl acetate, butyl propionate or butyl acetate are used. The thinners are generally mixtures of solvents of approximately the same composition as the liquid, but in such a case as the first liquid described a cheaper thinner can be used for almost all the year with resulting economy. Such a thinner could be made with 35 per cent butyl acetate, 10 per cent butanol, 10 per

cent ethyl acetate, 10 per cent benzol and 35 per cent toluol or solvent naphtha.

In mixing bronze powder with bronzing liquids it is good practice to add a small amount of thinner to the powder first, to eliminate air bubbles, and then add the bronzing liquid and thinner in the required proportions for the pressure and type of spray gun used.

### Leather Dopes.

The making of artificial leather, started by Wilson and Story in 1882, consumes vast quantities of pyroxylin solutions. Many of the largest users make their own, but some buy what are called leather dopes which they mix with oils and pigments in the factory. The purpose of these dopes is to permit of the building up on the canvas or other cloth a strong, durable, flexible film of pyroxylin and oil which, when embossed to give the leather grain, will serve as an excellent substitute for real leather.

Leather dopes are generally applied by a blunt knife operated by machine. For this reason they are made rather viscous. The manipulation of solvent formulae to give the desired qualities together with cheapness is a very specialized art and each manufacturer cherishes what he conceives to be the best formula. Much scrap celluloid and film is used.

Since many coats, 3 to 30, are applied it is probably economical to use a low-grade dope for the intermediate coats and a high-grade one for the first two and the last two or three. With modern high concentrations of cotton it seems reasonable that the number of coats will be sharply reduced, inasmuch as a blend of pyroxylin solutions can be made that will leave five times the film content of the early high viscosity dopes, and still have sufficient mobility for application. The saving for each eliminated application is considerable, for as has been before mentioned the bulk of the cost of a lacquer is the solvent, and especially so when high grade liquids are used.

**Leather Dopes. Artificial Leather. Split Leather.**

One of the earliest, and still one of the largest uses of pyroxylin solutions is in the making of artificial leather, split leather and patent leather. Solutions for these purposes are called leather dopes, and in general are quite analogous to the airplane dopes used for covering airplane wing fabrics.

The manufacture of artificial leather is no longer an infant industry and several large firms are making this product under the names of Fabrikoid, Keratol, Zapon, etc. It is widely used for book-covers, automobile seats and cushions (Henry Ford is the largest producer of the commodity in the country), furniture upholstery and hundreds of other minor uses. Besides cheapness, artificial leather offers a uniformity of thickness and quality unobtainable in natural leather, and it can be obtained in rolls of any desired width and length.

Pyroxylin artificial leather is made from a cotton fabric upon which has been built up a plurality of coats of mixtures of oils, pyroxylin and plasticisers together with pigments to give the desired color. When the desired thickness has been attained the material is run through an embossing machine where under the proper conditions the desired grain effect is impressed into the fabric. If a hard finish is desired, a nitro-cellulose coating with a minimum of oil is applied as a final measure. The problems of the industry are mostly of a mechanical and engineering nature, for not only is the material made by machinery, but in its applications it is used in machines wherein rigid specifications of dimensions, plasticity, etc., must be adhered to. When it is considered that the basic fabric itself intrudes problems in weight, closeness of weave, sizing, dyeing, etc., that each coat of dope is applied by a knife set to give a definite thickness provided that the viscosity and solid content of the dope as well as the temperature are kept constant, that in the embossing alone there are the three variables of pressure, temperature and time, that colors must be matched and kept uniform and that all this must be done with

pyroxylin, pigments and oils which are subject to wide variations, it can be seen what close control and engineering ingenuity must be employed. We may add that since the industry is highly competitive it is necessary to keep all costs rigidly reduced to the minimum.

The larger manufacturers start with the pyroxylin and carry on all subsequent steps of solution, filtration, incorporating with oils and pigments, etc., in their own plants. The smaller users buy a dope of the desired properties, incorporate their oils and pigments and then proceed with the manufacture.

The pyroxylin used is generally that of the 30- to 60-second variety. An 8 oz. solution was the customary concentration. As the actual film content of such a solution would require far too many coats to build up to the desired thickness, oils were added from the very beginnings of the industry. Boiled or blown linseed oil, rapeseed oil and castor oil are used to the largest extent, while soya-bean, perilla and cottonseed oil have been experimented with. A certain amount of plasticiser of a solvent nature seems necessary, and 2 to 5 per cent of camphor is frequently used. Acetanilid has found some value as a camphor substitute in this industry, while the usual pyroxylin softeners such as tricresylphosphate or butyl tartrate would seem to be indicated as camphor substitutes.

The pigments are ground in castor oil, usually in a roller mill, and added to the dope, the grinding and mixing being outlined in the discussion of enamels in this volume. The cheapest pigments are used.

As solvents amyl acetate and acetone oils were first used. The first became too expensive and the second had too disagreeable and lasting an odor for commercial success. As competition increased the industry swung over more or less completely to the cheapest mixtures, such as ethyl acetate and alcohol or benzol. To avoid blushing with these low-boiling solvents, and to secure greater speed of production, forced drying under heated drying-tunnels was adopted, a temperature of about 150° to 200° F. being used.

The thickness of each coat and the number of coats depends on the type of fabric desired; the former is controlled by the initial composition of the dope and by the adjustment of the knife that levels off the excess dope. Having determined the formula and the number of coats desired, the maker passes his roll of fabric, dyed to the proper shade, through a machine where it is coated with the dope, then through the drying tunnel where it is dried rapidly and then the procedure is repeated till the required number of coats have been applied. It is next embossed under predetermined conditions of pattern temperature and pressure of the embossing machine, and time of contact. Finally a thin coat of high viscosity (100 to 200 sec.) pyroxylin is applied and the material dried, wound on rolls and sold.

From 1 to 1½ pounds of oil are used per pound dry pyroxylin in most of the coats, although the first and sometimes the second anchorage coats are generally lower in oil and pigment, thus giving a more firm and durable adhesion to the cloth.

The practical difficulties are many. A typical defect is pinholing, which may come from air trapped in the cloth or from too rapid an evaporation of solvent. Changes in viscosity due to temperature changes often cause much trouble, both in grinding pigments and in controlling the spread of the dope by the knife. Fires are of frequent occurrence, due to static electricity generated and stored on the moving belts, etc. Grounding of metal parts and humidification of the atmosphere are used as precautions.

#### FORMULAE. ARTIFICIAL LEATHER DOPES

##### High Grade. (For hand finishing)

8 oz. pyroxylin (30-40 sec.)
2 pts. butyl acetate
1 pt. amyl acetate
1 pt. butanol
2 qts. toluol or solvent naphtha
1 oz. acetanilid
2 oz. camphor

##### Cheap

26 oz. pyroxylin
2 pts. ethyl acetate
1 pt. methyl acetone
1 pt. denatured alcohol
4 pts. benzol
2 oz. camphor

To be Mixed with Oils as Described

High-bodied Dope	Doerflinger's Dopes (U. S. Patent 1,320,458)
6 oz. pyroxylin (60-80 sec.)	6 oz. pyroxylin
30 oz. pyroxylin ( $\frac{1}{2}$ sec.)	28% methyl acetone
1 pt. butyl acetate	5% diacetone alcohol
2 pts. ethyl acetate	25% butanol
1 pt. denatured alcohol	42% benzol
3 pts. benzol	6 oz. castor oil
1 pt. toluol	
3 oz. camphor	
	8 oz. pyroxylin
	30% ethyl acetate
	4% diacetone alcohol
	16% butanol
	50% benzol
	16 oz. boiled rapeseed oil

Camphor may be supplied by using scrap celluloid, which generally contains 75% pyroxylin, and 25% of camphor.

### Split Leather.

This material is made somewhat similarly to artificial leather, but with certain fundamental differences. In the first place, the basic fabric is a split, or thin inner section of the hide after the grained outer portion has been removed. In itself the split has little merit, being porous, weak and devoid of grain. When treated with pyroxylin and oil solutions, however, a great improvement in strength, durability and finish can be obtained, and such leather is used in great quantities for hand-bags, book coverings, cheap gloves and many other places where it supplants real outer grain leather. It has an advantage over artificial leather in that it can be called leather without technically misbranding it.

Since the splits, which follow the form of the hides, are irregular in size and shape, the application of dopes to them is usually done by hand. A swab or a brush  $2\frac{1}{2}$  inches by 6 inches is generally used. Since the material is brushed, it is necessary to use solvents of much higher boiling point than in the case of artificial leather, and amyl and butyl acetates, fusel oil and butanol are frequent ingredients. The extra cost of solvent and of the primary split is somewhat counterbalanced by the fact that only three coats are usually given,

whereas six to thirty coats are required in artificial leather manufacture.

A typical procedure for black split leather is as follows. A solution containing 8 to 12 ounces of pyroxylin and about 3 pounds of castor or boiled rapeseed oil to a gallon, colored with  $\frac{3}{4}$  ounce spirit soluble nigrosine per gallon is spread on the dried hide, which is then hung up and allowed to dry overnight. The second coat contains only 2 pounds of oil to 10 ounces of pyroxylin, while the third coat runs 6 ounces of oil to 12 ounces of pyroxylin. After this is dry the desired grain is embossed in the fabric, a finishing varnish to preserve and increase the gloss applied consisting of clear pyroxylin with a minimum of oil, and averaging 2 oz. pyroxylin to a gallon.

In the making of patent leather a somewhat similar procedure is used, but every effort is bent to securing a smooth glossy black surface. The dried coats are pumiced smooth and the dope flowed on so as to avoid brush-marks. Boiled linseed oil is generally used, with 1 to 2 times its weight of pyroxylin dissolved in a high-grade solvent such as butyl acetate 25 per cent, butanol 20 per cent, toluol 55 per cent. The oil is first dissolved in one-fifth its weight of ethyl or butyl acetates, and the pyroxylin solution added to it slowly with constant stirring. A solution of nigrosine in similar solvents is made and added to give the desired color—about 2 oz. per gallon of nigrosine being generally used. The boiled oil appreciably increases the viscosity of the solution.

Similar products are made by enameling paper in an analogous way, and this finds some use in wall-papers, ornamental paper and catalogue and similar covers. Recently a fabric impregnated with pyroxylin has been placed on the market as a cloth for window shades which can be cleaned with soap and water. It is probably an improvement over the older type of shade, but it is a question whether the cost can be reduced to a saleable level.

The recovery of the solvents used in the artificial leather and similar industries seems feasible, but as far as known

few firms are taking advantage of its possibilities for economy. The hot air from the drying tunnels, containing the vapor of various esters, alcohols and hydrocarbons in a very dilute form, do not make an appetizing subject for solvent recovery, but if solved the gain would be considerable. Even in the cheapest dope the cost of the solvent is a good fraction of the total cost and further reductions in this seem only possible by some means of recovery. Compression and refrigeration seem out of the question from an economical basis, but some absorption method such as the use of silica gel or of the Bregeat system of cresol scrubbers might be feasible. If only a single solvent were used this would be much simpler, but it is a question as to whether any system would return a mixture even approximately the same as the original. The reader is referred to the monograph by C. S. Robinson on The Recovery of Volatile Solvents (Chemical Catalog Co., N. Y.) for detailed information along this line.

### Airplane and Airship Dopes.

During the war great quantities of pyroxylin solutions were used in the manufacture of airplanes and airships. The cotton or linen wings of the planes were treated with several coats of clear lacquer, which not only served the purpose of making the fabric water-proof but also by virtue of the contractile power of pyroxylin solutions tautened the fabric and markedly increased its tensile strength. The type of dope used for this purpose differs markedly from leather dopes, in that only the minimum of softener is used.

A typical formula is given in Navy Department Specifications 49D2, for Nitrate Dope for Aircraft Use.

8 oz. pyroxylin.  
1 gallon solvent.

The solvent consists of the following ingredients:

	Per cent		Per cent
Ethyl acetate .....	44	Denatured Alc. ....	2
Amyl or Butyl acetate ....	22	Benzol .....	32

This mixture is obviously too rich for economy and more recent specifications, 49D4, do not particularize the solvent except that it must permit of the material being sprayed or brushed without blushing at a humidity of 80% at 20° C. The other requirements as to total solids, acidity, durability, etc., are set forth in the specifications. No tetrachlorethane or similar toxic ingredient is permitted.

Most of the planes are finished with aluminum powder suspended in a clear lacquer, generally of a higher quality than the dope. Pigmented dopes, red, white, blue, yellow and khaki, are used as insignia and marking enamels, although these are sometimes made on a varnish base.

The first coat on the wings is frequently a cellulose acetate film, apparently chosen because of its non-inflammability.

The rubberized fabric composing the gas-bags of airships is also treated with pyroxylin dope. Specifications 49D1 require the following.

	<i>Per cent by Weight</i>		<i>Per cent by Weight</i>
Amyl acetate .....	21	Denatured Alc .....	2
Butyl acetate .....	36	Castor oil .....	8
62° Gasoline .....	28	Pyroxylin .....	5

The denatured alcohol is the No. 44 formula, containing 10 gallons of butanol to 100 gallons of grain alcohol. The castor oil is of the cold-pressed variety. The material must be of less than one-tenth of one per cent acidity as acetic acid, so that one pound of aluminum powder may be mixed with each gallon of dope without gel formation. The purpose of the dope is to reduce the rate of diffusion of the gas, whether hydrogen or helium, through the gas envelope.

A solvent used for removing old dope from wings is specified in 49S4, and consist of the following formula :

	<i>Per cent by Volume</i>		<i>Per cent by Volume</i>
Methyl acetate .....	35	Acetone oil .....	15
Methyl acetone .....	35	Crystallizable benzol ....	15

### Pyroxylin Cements.

For many purposes, especially for uniting leather surfaces such as belting, pyroxylin cements are used. These are generally 8-ounce, high viscosity pyroxylin solutions, in cheap, rapidly evaporating solvents. Such a formula would be 8 oz. pyroxylin, 1 oz. ester gum, 2 oz. castor oil in a solvent composed of 25 per cent ethyl acetate, 20 per cent denatured alcohol, 5 per cent butyl acetate and 50 per cent benzol. In applying these cements it is generally advisable to put a thinned coat on first which will fill the pores and supply an anchorage for the subsequent heavy coat. The cemented parts are pressed together and after a short while give a very firm, durable and waterproof union.

### Nail Polishes and Corn Cures.

These are also solutions of pyroxylin, generally in mixtures of esters and alcohols to avoid the unpleasant hydrocarbon action on the body. An 8-ounce pyroxylin solution in a mixture of 25 per cent butyl acetate, 20 per cent butanol, 15 per cent ethyl acetate and 40 per cent denatured alcohol characterizes them. They generally contain about 1 oz. dammar to a gallon, and in the case of nail polishes a trace of pink dye. The corn cures contain a small amount of salicylic acid and occasionally Indian hemp to a gallon.

### Collodion.

Pharmaceutical collodion still consists of 8 oz. pyroxylin dissolved in 3 parts ether and 1 part alcohol. Proprietary substitutes are using amyl and butyl acetate solutions, giving a better product. As plasticiser for flexible collodion 3 ounces camphor and 2 ounces castor oil are used.

**RECENT DEVELOPMENTS IN LEATHER LACQUERS**

Besides the use of pyroxylin lacquers in the artificial leather, split leather, and patent leather industries a new application of pyroxylin finishes has recently begun to attract attention. This is the finishing of light leathers comprising shoe leathers, such as chrome-tanned goat, sheep, calf and cow-hides; and fancy leathers, such as vegetable tanned skivers, sheepskin, pigskin, sealskin, etc., which are used for such purposes as handbags, sweat-bands, shoe-linings, etc.

Up to the present time these leathers have been finished by dyeing them with aniline dyes and then applying a watery solution or emulsion of such materials as casein, gelatin albumens, waxes or shellac colored with dyestuffs and finely ground pigments. These finishes succeed in levelling the color and obscuring the natural unevenness and defects in the skins, without unduly hiding the natural appearance of the grain. On the other hand, these materials give a finish that is not so satisfactorily fast to rubbing and moisture and for a long time work has been carried on to replace them with nitro-cellulose lacquers.

This is by no means an easy problem, as the number of failures scored by lacquer makers indicates. A lacquer for this purpose must have the usual requirements of adhesion, elasticity and flexibility, must be able to conquer the different grain structures presented by the varying nature of skins and their tannage, must be able to withstand the severe mechanical operations of glazing and embossing, and lastly but most important, must be colored so as to secure the levelling effects, true shades, and fastness to light.

Pigments have not been successful, as they give a similarity to artificial leather that is not desirable. Dyes hitherto obtainable have not been fast enough to light. Within the past few years, however, dyes of a very unusual type have been developed abroad, which are light-fast and non-obscuring, and in

conjunction with properly plasticised lacquer solutions have made strong headway in the European leather industry and are beginning to be of importance here. The composition of these materials is unknown to the author but the effects he has been privileged to see are very attractive.

## CHAPTER IX

### METAL AND WOOD LACQUERS

One of the first and most extensive uses of spirit varnishes was to protect such tarnishable metals as silver or brass by applying a thin film of clear gum over the surface. These films were of value, but are to-day being superseded in great measure by the pyroxylin lacquers, which are harder, more durable, less highly colored and less corrosive. In the electro-plating industry, in the vast brass working industries, in silverware manufacture and even in the making of fine tools and steel hardware where objects of value may rust, pyroxylin metal lacquers are being consumed in enormous quantities.

The function of such a lacquer is primarily to protect the metal, but in many cases it is used to enhance the gloss and often, especially in the brass bed industry to give a richer color to the brass. Since the copper in brass is the more valuable component, and since the quality of brass is judged by the richness of its hue, many makers have found it profitable to use a high zinc, pale brass and lacquer it with a pyroxylin solution containing such dyestuffs as the Sudan yellows which are permanent and high in color. The same is done by many makers of scientific instruments such as microscopes and telescopes. A pure pyroxylin lacquer gives a matt finish, and where a brighter gloss is required gums in various percentages are mixed with the pyroxylin. The presence of gums increases adhesion, but decreases the toughness somewhat.

Since only a thin film is desired, metal lacquers are diluted as much as possible, to the point where the film is so thin that iridescence is just barely prevented. They should therefore

contain as much body as possible for the price and the addition of dammar or shellac permits of this.

The lacquers used for metal must be acid free, unblemished by specks or cloudiness, and of such a quality that blushing will not occur. Any imperfection in a film shows up on a polished metal surface so an attempt to cheapen the product is risky. The pyroxylin should be of the highest grade, especially for the silver lacquers where nitrated tissue paper is often employed. Acidity or high color should cause the rejection of pyroxylin for this purpose. The solvents also should be as near to water white as possible and the clarification accomplished by the filter centrifuge. The finished lacquer should be flowed on a clean glass plate and carefully scrutinized under a lens for dust or dirt particles. These precautions may seem over-meticulous, but the large users of this type of material buy under very rigid specifications that must be adhered to. Of course even a cheap bronzing liquid may be used as a metal lacquer, but even if it does not blush the film is almost certain to be wavy or pebbly and detracts from the polished beauty of the metal instead of enhancing it.

Lacquers for brass often contain high percentages of gum, but silver lacquers are generally clear pyroxylin with a very small amount of the palest dammar to give adhesion. Where much flexibility is required, say in brass articles that are to be sheared or bent after lacquering, tricresyl phosphate is added.

In this class come the priming lacquers used on metal surfaces of steel, iron or aluminum whereon enamels are to be applied, such as steel office furniture or automobile bodies. These generally contain considerable quantities of resins which give the primer adhesion to metal. The enamel should then contain only a minimum of those solvents which act on the resin, for the desideratum is that the enamel coat only amalgamate with the surface of the primer and not penetrate throughout.

A clear lacquer requires a clean surface. This is often overlooked by sprayers and thus trouble is encountered that

is generally blamed on the material as a convenient scapegoat. Grease or oil will ruin the adhesion of any pyroxylin product to the metal and water or plating liquid is about as bad. The articles to be lacquered should be scoured, burnished and dipped in benzine before being sprayed or dipped in the lacquer. Moreover a dusty or dirty finishing room nullifies all the care taken in making the lacquer.

There are so-called water dip lacquers, in which plated articles can be placed directly from the plating bath, but these contain no pyroxylin and are generally composed of copal, rosin or ester gum dissolved in petroleum naphtha. Water is immiscible with this solvent and sinks to the bottom, from which it can be drawn off periodically. However, the resulting film of rosin or ester gum has practically no value except as a very temporary protective film.

Dipping is rapidly going out of fashion with the improvement in present spraying equipment. It never was really economical when the frequent spoilages of the dipping liquid through accidental impurity or fire are considered, and where intricate designs were to be lacquered the coating was always imperfect. The spray gun is a much better method and it is to be hoped that it will become universal, except with such objects as broom-handles and lead pencils whose shape lends itself ideally to the dipping process. Brushing is possible on small articles with a high grade lacquer, and where only a few articles are to be treated is probably the only sensible method. For any volume production, however, the hand brush is far too slow.

The pyroxylin used in these lacquers is generally the so-called lacquer cotton, of about 30-second viscosity and is a better product than the dope cotton or bronzing liquid cottons of higher viscosity. Only dammar or shellac gums should be used, as the color of the others is somewhat too dark. The dammar or shellac (bleached, wax free, bone dry, dissolved in butanol) should be tested for acidity before using in metal lacquers.

Some formulae that have been successfully used follow:

**High Grade Silver Lacquer**

8 oz. pyroxylin  
3 pts. butyl acetate  
1 pt. butanol  
4 pts. toluol  
1 oz. tricresyl phosphate.

**Medium Grade**

8 oz. pyroxylin  
1½ pts. ethyl acetate  
¼ pt. dammar solution  
½ pt. butyl acetate  
¾ pt. butyl propionate  
1 pt. butanol  
2 pts. toluol  
2 pts. benzol.

**High Grade Brass Lacquer**

8 oz. pyroxylin  
1½ pts. dammar solution  
2½ pts. butyl acetate  
1 pt. butanol  
4 pts. toluol

**Flexible Brass Lacquer**

8 oz. pyroxylin  
1 pt. ethyl acetate  
¼ pint bleached shellac in butanol  
1½ pts. butyl acetate  
¾ pint butanol  
¼ pt. elemi solution  
2¼ pints toluol  
2 pts. benzol  
½ oz. dibutyl phthalate

**PRIMING LACQUERS**

**For Steels, Cast Iron, etc.**

8 oz. pyroxylin  
½ pt. dammar solution  
¼ pt. ester gum solution  
¼ pt. elemi solution  
1 pt. ethyl acetate  
1 pt. butyl acetate  
½ pt. butanol  
½ pt. denatured alcohol  
2 pts. benzol  
2 pts. toluol

**For Aluminum, White Metal, Glass, Zinc**

6 oz. lacquer pyroxylin  
6 oz. ½ sec. pyroxylin  
½ pt. shellac solution  
1 pt. ethyl acetate  
1 pt. butyl acetate  
½ pt. butanol  
½ pt. denatured alcohol  
2½ pts. toluol  
2 pts. benzol  
2 oz. tricresyl phosphate

**Finishing Lacquers.**

After an article has been lacquered, either with bronze or enamels, it is often considered desirable to cover with a finishing lacquer. By doing this the durability of the undercoat is heightened and a fine gloss given to the bronze or enamel. It

is requisite that the undercoat be smooth, as the top coat's smoothness or brightness depends on this in great measure. A finishing coat is generally of the metal lacquer type, but the best ones are made with a considerably higher percentage of pyroxylin, the low viscosity type being used. Thus a coat of appreciable depth can be applied, with consequent enhanced beauty and durability. Unless the solvent mixture is of high grade the top coat will be streaky, wavy, or possess the self-descriptive "orange-peel effect." For application over bronze or dark enamels a slightly yellow finishing lacquer can be used, but over aluminum, or white enamels the highest grade of pyroxylin and the palest gums should be used to avoid the frequent yellowing of the white after the application of the top-coat.

Finishing lacquers are made in dull or matt, semi-matt, and gloss types. The latter contain resins in considerable amounts and while necessary where gloss is required to the highest degree are always less hard and durable than the matt finishes which contain only small amounts of resin. A much better product can be made by using two coats of finishing lacquer, the first of the gloss type and the second a matt, but this is generally too expensive for manufacturing economy. Many spray men have acquired the habit of using a finishing lacquer in conjunction with their enamels, adding up to equal parts of the lacquer to the enamel and then thinning to spraying consistency. It is obvious that lacquers for this purpose should be as little viscous as possible, for otherwise the coverage of the blend will be very low. This admixture of lacquer should not be required, inasmuch as a high grade enamel will already have incorporated in it the proper amounts of pyroxylin and gum. However, experience has taught the sprayers that the cheap enamels, while having good coverage, are not of satisfactory adhesion unless fortified up with the lacquer, which also improves the flowing qualities due to its containing more high-boiling solvents. The method is wasteful of solvent, and it would be better practice to use a high-grade enamel at the

start, but it is difficult to convince spray men of this and most manufacturers simply make up the solutions the user has been accustomed to and reserve their better grade of material for newer and more progressive lines such as the automobile industry.

For production of a gloss on the usual satin-finished pyroxylin enamels a finishing coat of the semi-gloss type gives a much better product than the one-coat gloss enamels, and wherever the expense is warranted by the selling price of the article it should be done. The gloss enamels not only dry more slowly and deteriorate more rapidly, but their gloss is seldom long-lived and the softer top surface makes smudging and scratching much more common. Eventual brittleness due to the high gum content is another drawback.

#### FINISHING LACQUER FORMULAE

Matt Finish	Gloss Finish
6 oz. lacquer pyroxylin	6 oz. lacquer pyroxylin
8 oz. $\frac{1}{2}$ sec. pyroxylin	6 oz. $\frac{1}{2}$ sec. pyroxylin
$\frac{1}{2}$ pt. dammar solution	1 pint dammar solution
2 pts. butyl acetate	$\frac{1}{2}$ pt. shellac solution
$\frac{1}{2}$ pt. butyl propionate	$\frac{1}{2}$ pt. ethyl acetate
1 pt. butanol	1 $\frac{1}{2}$ pts. butyl acetate
4 $\frac{1}{2}$ pts. toluol	1 pt. butanol
2 oz. butyl tartrate or dibutyl phthalate	$\frac{1}{2}$ pt. butyl propionate
	1 oz. dibutyl phthalate
	3 pts. toluol
Cheaper Lacquer (for dark enamels)	
6 oz. lacquer pyroxylin	
6 oz. $\frac{1}{2}$ sec. pyroxylin	
1 pt. ester gum solution (6 lb.)	
1 $\frac{1}{2}$ pts. butyl acetate	
$\frac{1}{2}$ pt. ethyl acetate	
$\frac{1}{2}$ pt. butanol	
$\frac{1}{2}$ pt. denatured alcohol	
4 pts. toluol	
2 oz. castor oil	

For use over enamels, especially those which contain lakes, it has been found advisable to add a small amount, 10 to 20 per cent, of the enamel to the finishing lacquer. This prevents the change in color of the enamel coat that is so often witnessed. If white enamel is used as an undercoat, a small amount of it in the top coat will overcome any slight yellowness, in the lacquer.

### Wood Lacquers.

The importance of wood lacquers, or rather pyroxylin varnishes, is of recent growth. While pyroxylin solutions had been used for a long time to cover small wood pieces, the fact that any real finish would require a huge multiplicity of coats made it far too expensive for the average wood worker. With the advent of low viscosity pyroxylin, and of cheaper high-grade solvents it has become possible to give with two or three coats a finish that far excels varnish in its speed of application and drying, hardness, resistance to water and alcohol, and which, although of lower gloss than unrubbed varnish, is of a beautiful satin luster that is now generally considered far more attractive on furniture than the flashy gloss given by shellac or varnish.

The first requisite of a pyroxylin varnish is high body, for wood is notably porous and absorbent and requires a considerable amount of solid film before the grain is no longer apparent to the touch. The beauty of a wood finish is in great measure due to the depth of the film which a practiced eye can judge by an oblique glance across the surface, and a mere covering of the grain with a smooth surface is only a minimum requirement by the discriminating purchaser of fine furniture. A second essential requirement is that the varnish shall flow smoothly when sprayed and not wrinkle up or pucker as some do. This end is generally obtained by means of a proper percentage of alcohols such as butanol and to some extent by amyl acetate and butyl propionate.

Many pyroxylin wood lacquers are in reality gum lacquers

with a small amount of pyroxylin, and these should not be classified with the high-grade varnishes consisting mostly of pyroxylin with a lesser proportion of high-grade resins to give increased body and gloss. The former lacquers are naturally much cheaper, but of greatly decreased hardness, durability and beauty.

An effect frequently met with is that of pinholing, due either to imperfect filling of the wood or to the evaporation of low boiling solvents. This leaves groups of tiny holes throughout the wood and absolutely ruins the finish. A high-grade material, on properly filled and seasoned wood, will not do this, but often cheaper lacquers and thinners are used with success in the winter months and their use continued through the humid periods with lamentable results. It is justifiable economy to use the cheaper lacquers when weather conditions permit, but provision should be made for switching to the better grade when bad weather sets in. It is not always advisable to add fortifier to the cheaper mixtures, as the low-boilers are still in the lacquer and may cause pin-holing even if blushing is prevented. It also disturbs the proper balance between the constituents of the solution and causes an irregular surface. It is true that an expert sprayer can overcome these difficulties to a large extent, but it is safer and preferable to use the better lacquer.

A most important point is the preparation of the wood. It should be well seasoned and planed and sandpapered to a smooth surface. The grain should be filled and herein the user runs into a bewildering variety of fillers from which to choose. The oil fillers are not desirable under pyroxylin, owing to the solvent action of the mixture on the oil. The paste fillers, containing such transparent solids as whiting and silica made into a paste with a minimum amount of oil and drier have been used to good advantage. These fillers are often stained with umber, ochre or dyes to give the effect of the desired wood, and can be purchased ready for use after thinning with a little turpentine or naphtha. They are generally brushed on, al-

lowed to remain for 15 to 30 minutes, the excess wiped off with a cloth and the surface then sandpapered down to the wood. One coat of filler is generally sufficient, although open grain woods such as oak or chestnut often require a coat of shellac as a sealer on the filler. Shellac seems to afford an excellent first coat in many cases and after rubbing down with pumice and water can be used to anchor a second and third coat of the pyroxylin, with a slight economy. However, most users prefer to give two or three pyroxylin coats directly on the filler, these coats either containing a dye to simulate mahogany, walnut, cherry or other cabinet woods, or being clear solutions which when applied on the stained filler give the desired effect.

Water fillers are coming into some use in connection with pyroxylin varnishes, as the binder, generally gelatine or casein, is insoluble in the lacquer solvents and thus does not lift up or peel as the others sometimes do. A precaution with water fillers is to be sure that they are dry before the lacquer is applied, as residual water is detrimental to the film.

Pyroxylin surfaces are very hard and to facilitate smoothing them special sandpapers have been developed. These use silicon carbide and aluminous oxide, artificial abrasives, bonded to the paper by a waterproof and oil-proof glue, for the better grades, and garnet or flint for the cheaper varieties. These are generally used soaked in water or oil, either petroleum oils or special compounds being used, but for some purposes they are used dry. Manning Grits and wet or dry papers are the best known brands, and they come in various degrees of fineness, depending on whether the purpose is to clean off rough metal or to give final fine sanding to a top coat with many grades in between.

The first coat of pyroxylin lacquer is generally rough, as tiny fibers in the wood become coated with the material and stand up stiffly from the surface. This coat is allowed to dry for 4-8 hours, a longer time being helpful, and is then rubbed down with a medium grits till smooth. The second coat is

sometimes sanded, but this is generally unnecessary. The third coat, or the second if only two are used, is rubbed down with a very fine paper and then polished with pumice stone and oil. A final polishing with wax is often given the surface, and results in a more shiny surface that, while not durable, is still sufficient to catch the eye of the ultimate consumer.

Allowing two or three hours between coats it is a simple matter to finish radio or phonograph cabinets or similar furniture in a day, and work commenced in the morning is often shipped in the late afternoon. Such speed, combined with the high quality of the finish is a phenomenon to which cabinet makers and furniture dealers are only just becoming accustomed.

Some trouble has been experienced by purchasers of wood lacquer because the manufacturer, in his anxiety to secure a hard product, has omitted a proper plasticisation of the solution. When weather conditions, or the gradual warping of insufficiently seasoned wood causes an expansion or contraction of the finished piece the brittle pyroxylin crumbled away and this has placed the lacquers in bad odor with some users. Another cause of difficulty has been the use of the same fillers that they used with oil varnish, and trouble due to this cause has also been unjustly laid at the doors of the pyroxylin varnish.

Some makers have had much success with lacquer as an undercoat for a suitable oil varnish.

Furniture of the very highest grade, such as pianos, is now being successfully finished in lacquer under what is almost a varnish schedule, namely 1 or 2 days between coats and a week or more before rubbing and polishing. What is lost in speed is gained in beauty and durability of finish.

A serious defect in wood finishes is what is called "printing," by which is meant the deformation of the film due to pressure before the film has set to its maximum hardness. With oil varnishes weeks are often required before the pro-

longed pressure even of the thumb or finger fails to show the imprint on the surface, while there are very few varnishes which at any time will bear up under more than 300 to 400 pounds per square foot pressure. A good pyroxylin film will withstand a pressure of over 800 pounds within a few days after application, while sufficient hardness to permit of wrapping and shipping is often achieved in a few hours. This quick drying also eliminates another bugaboo of the finisher, the catching of dust particles by the film while still tacky. It is apparent that a varnish that remains soft for a day or two will be in graver danger of being ruined by dust than one that dries in a few hours. A third feature of importance is that while many varnishes have a tendency to become sticky in hot weather, pyroxylin does not, an obviously desirable attribute in chairs and benches used in summer months. Lastly, while most varnishes when scratched turn white along the line of the mark, a pyroxylin film is not only harder to scratch, but if this is done by a sharp point the scratch will not be white and thus is less noticeable.

The drawback to pyroxylin lacquers for wood is the price, which in cases of large production and quick turnover is more than balanced by the economy in time, labor and overhead, but in plants where small quantities of high-grade merchandise are produced and in those making very cheap articles where the finish is merely nominal is too high for the purpose. Car-loads of pyroxylin wood lacquer are being used weekly, and it is certain that it will be utilized more and more as the wood-finishers realize its advantage and as the price reaches a point comparable with that of medium grade varnish.

In making wood lacquers, one point to be remembered is that while maximum body is obtained with the low viscosity pyroxylin, when these lacquers are sprayed on such objects as chair legs and arms and on most vertical objects a certain viscosity is desirable to avoid the running off of the lacquer from the surface with consequent sags and bare spots. To avoid this a small amount of high viscosity cotton is advan-

tageously used with the much larger amount of low viscosity material.

#### WOOD LACQUERS

High Grade	High Grade
20 ounces $\frac{1}{2}$ second cotton	15 ounces $\frac{1}{2}$ second cotton
6 ounces lacquer cotton	5 oz. lacquer cotton
$\frac{1}{2}$ pt. dammar solution	2 pts. dammar solution
$\frac{1}{2}$ pt. shellac in butanol	$\frac{3}{4}$ pt. ester gum
2 pts. butyl acetate	$\frac{1}{2}$ pt. ethyl acetate
$\frac{1}{2}$ pt. amyl acetate	1 pt. butyl acetate
1 pt. butanol	$1\frac{1}{4}$ pts. butanol
$3\frac{1}{2}$ pts. toluol	$2\frac{1}{2}$ pts. toluol
3 ounces dibutyl phthalate	3 ounces triresyl phosphate
$\frac{1}{4}$ ounce urea	$\frac{1}{4}$ ounce urea
Cheap Lacquer (will blush in humid weather)	
20 ounces $\frac{1}{2}$ second cotton	16 ounces. $\frac{1}{2}$ second cotton
5 oz. lacquer cotton	4 oz. lacquer cotton
1 pt. ester gum solution	1 pt. dammar
$\frac{1}{2}$ pt. dammar solution	2 pts. shellac
1 pt. ethyl acetate	$1\frac{1}{2}$ pts. butyl acetate
1 pt. butyl acetate	$3\frac{1}{2}$ pts. denatured alcohol
$\frac{1}{2}$ pt. butanol	2 oz. castor oil
$\frac{1}{2}$ pt. absolute alcohol	1 pt. methyl acetone
2 pts. toluol	The shellac is cut 4 pounds to a
$1\frac{1}{2}$ pts. benzol	gallon of 75% denatured alcohol
2 oz. castor oil	and 25% butanol.

Mixtures of Bismarck brown, nigrosine and chrysoidine dyes are generally used to color these lacquers. The dyes are dissolved to saturation in wood alcohol or denatured alcohol, filtered and mixed to give the desired shade. An ounce of Bismarck brown and half an ounce of nigrosine will give a light mahogany color to one of the above lacquers, and other colors can be made by varying the proportions. Some dye manufacturers make mixtures of dyes in the dry state which require merely solution and filtration to give the desired shade. Too much dye is liable to give a bronzy surface.

As stains under lacquer the water-soluble colors are preferred.

### Flat Lacquers.

Recently a very marked demand has arisen for the so-called "flat" or "satin" wood lacquers. These are wood lacquers in which small amounts of transparent pigments have been incorporated, so that the effect on the work is to give not a gloss, but a rubbed effect. As the use of this type of lacquer obviates in great measure the need for rubbing the lacquer, always an expensive operation, it has found a great field of usefulness. The finish is not quite as smooth and lustrous as a rubbed job, but closely approximates it. On intricate carvings and turnings where rubbing would be very expensive, it has proved a veritable boon.

The pigments used most generally for producing this effect are the stearates of magnesium, zinc and aluminum, usually ground into the lacquer in a pebble mill. Only a few ounces per gallon are needed and various sheens or degrees of gloss can be made by mixing different proportions of gloss and flat lacquer.

## CHAPTER X

### LACQUER ENAMELS

By lacquer enamels are meant pigmented lacquers which dry to an opaque colored surface. There is more confusion attendant upon the manufacture of these products than in any other pyroxylin product, because in addition to the usual variables we have the pigment to deal with, and this gives problems in choice of pigments, amount per gallon and method of grinding that makes the manufacture of really satisfactory lacquer enamels much more difficult than that of a bronzing liquid.

The purpose of enamels is to cover as much area as possible with a film that is opaque, of the desired color, as permanent as possible and as cheap as possible. Two types have evolved in the progress of the industry, the cheap variety and the high grade which cost from two to three times as much. The first is used in enormous quantities in the toy, lighting fixture, broom and similar industries where length of life of the finish is secondary compared to the initial appearance and cheapness. The high-grade material is used on steel furniture, automobiles, high-grade enameled wood furniture, bicycles and motorcycles, etc. The differences are primarily in the amount of pyroxylin and the quality of the solvents, although a real difference in choice of pigments appears. The high grade enamels, by the use of low viscosity pyroxylin and plenty of it, have a hardness and durability that make them adapted to the purpose for which they are sold. The cheaper enamels use scrap celluloid, film or cheap pyroxylin of high viscosity which deludes the purchaser into the belief he is getting more

for his money, cheaper solvents and plasticisers. For the price they give an excellent finish, but not to be compared with the higher quality enamels in appearance or durability.

The quality of the enamel depends very greatly upon the procedure used to incorporate the pigment with the lacquer base, and on the care and accuracy of the grinding depends whether a silky smooth lustrous film is obtained or one that is so rough that it is harsh to the touch and unpleasing to the eye. Moreover it must be realized that the coverage per pound of pigment is influenced by the fineness of grinding to a large extent, a pigment that is very finely comminuted and disseminated throughout a film being obviously of greater covering power than one that is segregated in larger agglomerations irregularly through the enamel coat. Despite this, some of the smaller manufacturers, in their haste to produce material turn out enamels which dry to a close approximation to sand-paper and which are only acceptable to the cheapest trade. It takes time and care to turn out high-grade enamels and the consumer should insist on this effort being made and the maximum smoothness achieved.

Occasionally roughness in enamels is due to other causes. Some makers use unfiltered pyroxylin for the purpose, and this is apt to contain fibers which do not grind easily and when stiffened by the dried lacquer give an effect similar to unground pigment. Another cause is the use of too low-boiling solvents, or incorrect spraying of the enamel, whereby a certain amount of the enamel dries in the air on its way from the spray gun to the surface and this dry enamel powder, the so-called "spray dust," settles on the surface and roughens it. There is no excuse for spray dust being deposited, however, as by adjustment of the distance from the nozzle and of the pressure any enamel can be applied in the wet condition.

The methods of incorporating pigments into the enamels may be considered under two headings. The first, and oldest method uses the common procedure in making varnish enamels and by it the pigment is ground in oil and added to

the lacquer in proper proportion. Castor oil is commonly used, although fusel oil has been mentioned by Worden and other authorities. Owing to the low viscosity and the high volatility of the latter its use does not seem logical and as far as known it is no longer practiced. There are several ways of grinding the pigment into the oil, for instance by the edge runners or chasers, by the flat stone mills and by the roller mill. The first two will be described briefly, but the third is the method now commonly adopted.

#### Edge-runner or Chaser Mill.

This is one of the simplest and most effective methods for grinding pigments in oil to a moderate degree of fineness. The chaser has a circular iron pan, the interior of which has been finished very smooth. Along the rim of the pan a heavy



FIG. 7.—Edge runner or chaser mill.

stone traveler of circular shape is moved by a bevel gear system from a central shaft. The traveler moves both along the rim of the pan and around its own axis. The pigment and oil are placed in the pan, the motor started and the combined motions of the traveler and the grinding between it and the pan serve to reduce the material to a homogeneous paste very

quickly. The most viscous material can be handled in this type of apparatus.

The pulley speed is generally 80 to 100 R.P.M. and the capacity of a machine with a 70-inch pan is about 400 pounds of paste. The traveler is equipped with a scraper to clean off the paste continuously and another scraper in the pan stirs up the paste and keeps it in the path of the traveler. Some types of chaser mills have two travelers, which naturally give a quicker grind.

The paste is drawn off through gates either in the bottom or the side of the pan. For certain types of fillers and glazes this type of machine is adequate but for pyroxylin enamels the stone-mill, three-roll mill and the ball mill are the standard types.

### **Flat Stone Mill.**

It is claimed by some ink and enamel manufacturers that the finest grinding can be done only by use of the water-cooled flat stone mill. In any event, an increased interest in this type of grinding device is being evidenced by enamel manufacturers.

The mill is reminiscent of the old mill-stones for flour grinding. Two buhrstone disks, mounted in metal, are grooved with a criss-cross pattern of parallel cuts, the markings on the upper stone being the reverse of those on the lower one. The upper stone is fixed, while the lower is rotated by a shaft and pulley or by direct electric drive. The material to be ground is fed from above through the center, and as the lower stone rotates is gradually forced out through the clearance space between the stones and is scraped off by a fixed knife into the receptacle. The combined rotation and cutting effect of the crossed grooves leads to a very fine grinding, and since these mills are generally arranged in tandem, with one pair of horizontal disks below the other, the final product is of very high quality. Various methods of water cooling to

avoid discoloration by the heat developed on grinding are used.

The common commercial size is one with stones 20 inches in diameter, which gives a daily output slightly less than the roller mill. The lower stone is rotated at about 40 R.P.M. for the large size and about 60 R.P.M. for the smaller sizes.

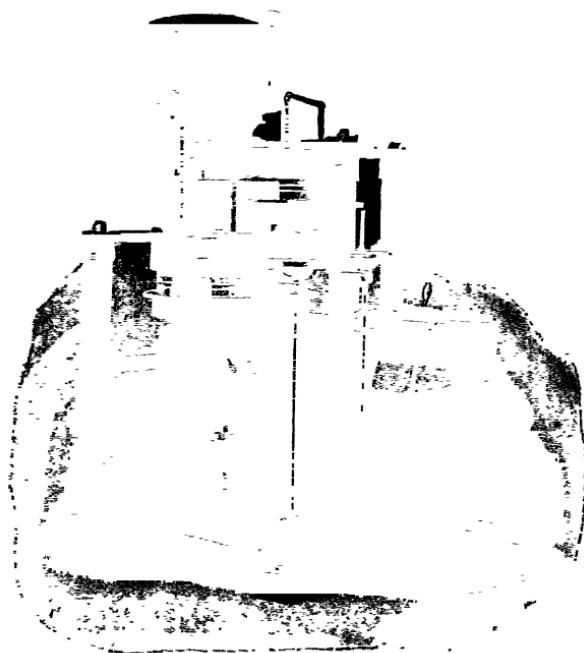


FIG. 8.—Stone mill.

A small sized laboratory mill is of great value in testing pigments and finds a wide-spread demand for the purpose. Very recently an enclosed stone mill has been developed which permits of grinding pigment directly into volatile vehicles such as pyroxylin solutions. This promises to be one of the best solutions to the lacquer enamel grinding problem.

### The Roller or Three-Roll Mill.

This very useful grinding device utilizes the combined crushing, grinding, twisting and shearing motions produced in a paste of pigment and vehicle by the action of three rollers moving at different speeds. The mill illustrated in Fig. 9 consists of three rolls of very hard chilled iron, firmly fixed in a solid framework, and provided with micrometer screws to secure a regulation of the distance between the rollers and

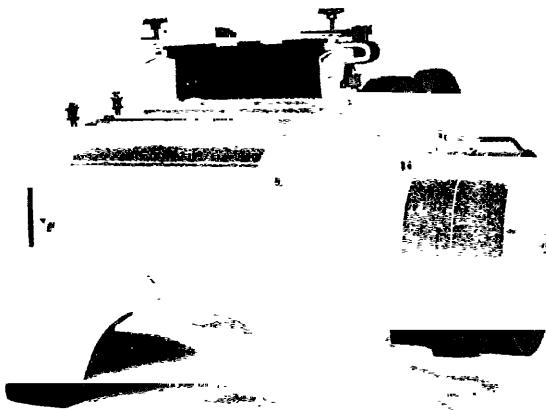


FIG. 9.—Three-roll mill.

with pipes whereby cooling water can be passed through the hollow cylinders.

The oil used for grinding lacquer enamel pastes is generally castor oil, or a mixture of this oil and solvent naphtha. The amount of oil per hundred pounds of pigment varies, being for the general run of pigments about 20 to 30 pounds, but running much higher for such pigments as prussian blue and carbon black. It is necessary to mix the oil and pigment to a crude paste before sending them to the rollers, and this is generally done in such mixers as the type illustrated in Fig. 10. A powerful parallel-blade agitator gives a rapid mixing

of the ingredients, which are then allowed to flow as a thick paste in between the first and second, or back and middle rollers, which have been carefully adjusted to give a fineness of grind depending on the pigment used and its original fineness. A battery of two mixers is often used, one being filled and agitated while the other is delivering its paste to the rollers, and economy of time is thus obtained. On the other hand, it sometimes is necessary to produce large quantities of one particular color such as black or white, and a set up

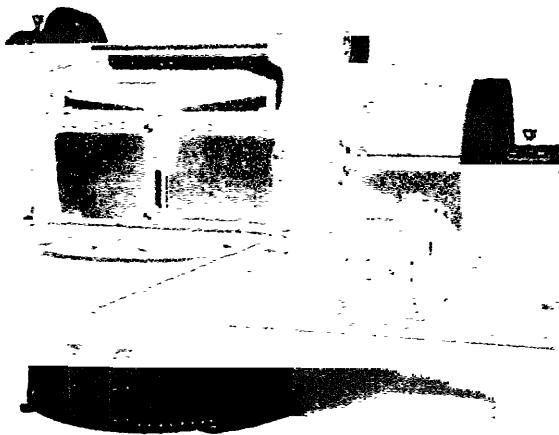


FIG. 10.—Mixer.

such as the mill and mixer diagrammed in Fig. 11 is used. Here one large mixer serves two roller mills and greater output and uniformity of product is thus obtained.

As has been said before, the rollers move at different speeds. The commercial units average a speed of 20 to 30 R.P.M. for the first or back roller, 40 to 60 for the second or middle roller and 80 to 120 for the third or end roller. The rollers are made with a slight taper at each end so that the coarser portions of the paste are pushed to the sides of the

delivery apron and are there scraped off by the operator and returned to the back-roller. A single running seldom grinds smoothly enough for pyroxylin enamels and two or three grindings with the rollers set closer together each time are generally used. A tandem arrangement where the material feeds from the apron of the first unit to the rear rollers of

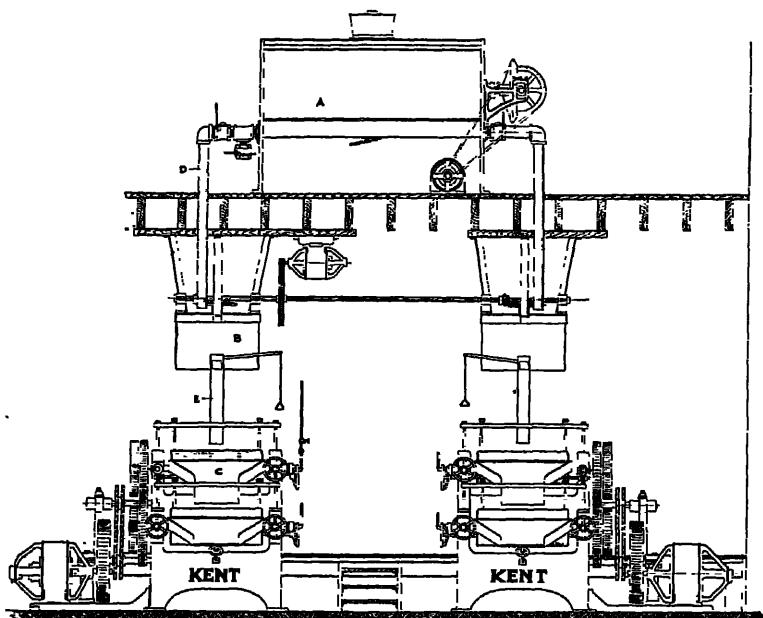


FIG. 11.—Mill and mixer.

the second is often used. A scraper removes the finished paste from the rolls, and it is run into barrels or cans for further treatment.

The usual plant size is 12 by 30 inches, that is, a unit with rollers 12 inches in diameter and 30 inches long. The output of such a unit, figured on a 9-hour day, runs between 800 and 1400 pounds of paste a day, depending on the fineness desired and the nature of the pigment. It is thus easily calculated that with equivalent investment in machinery the roller mill is

several times as productive as the pebble mill in point of time required per batch. The labor required is greater with the roller mill, as a pebble mill once loaded can be allowed to run without attention. The roller mill requires less careful adjustment of the charge and is less liable to spoilage by grit particles. Some of the largest producers of enamels use pebble mills with excellent success. Some others have had poor fortune with them and prefer the roller or stone mills.

The mills are generally run off line-shafting, by tight and loose pulley, or can be fitted for direct electric motor drive. They require considerable power, from 10 to 20 H.P. and a motor speed of about 1200 R.P.M.

The paste made as above is tested for fineness of grind by rubbing on a glass plate, or better still, by mixing a small quantity with lacquer in the proportion to be used in the large-scale mixing, and spraying the enamel on smooth tin. If satisfactory, the weighed amount is added to the pyroxylin and resin solution in any of several types of mixer, among which the pebble mill and the Kent airtight mixer seem to have found most favor. After thorough incorporation the enamel is run off into cans for the cheaper grades; or strained, centrifuged or otherwise clarified for the better class of products. The calculations are simple but errors are sometimes made. If a paste of 100 pounds pigment and 20 pounds of oil has been made, and it is desired to have one pound pigment to a gallon, it will require 1.2 pounds of the paste per finished gallon and involve the addition of 3.2 ounces of oil.

### **The Ball or Pebble Mill.**

Manufacturers of lacquer enamels have one difficulty to face in grinding that is absent or negligible in the paint and varnish industry. This is the evaporation of the volatile solvents in any of the open type mills which is not only wasteful but would create a great fire hazard and by constantly changing the concentration and viscosity of the enamel make it

impossible to secure uniform results. The use of an enclosed mill obviates these difficulties and the ball or pebble mill best suits the purpose of the lacquer enamel manufacturer.

The grinding action of these mills is due to the impact of the pebbles with which they are partly filled on particles of pigment and lacquer caught between other pebbles or the lining of the mill. The mills are generally run at 38 R.P.M. and in these revolutions the mass of pebbles is raised one half the diameter of the mill and falls, giving a combined pounding,

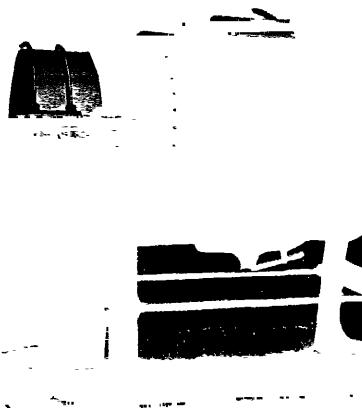


FIG. 12.—Pebble mill.

grinding and mixing action that produces under proper conditions a very high grade enamel that often can be emptied directly into cans or drums for shipment.

The pebble mill is essentially an iron cylindrical shell, carefully centered on shaft and trunnions so that it revolves easily. It is lined with buhrstone, flint or silex for the larger mills and with porcelain for the smaller sizes. The mill is half filled with pebbles, these being imported and carefully sorted so as to have an amorphous fracture and to be free from holes or other weakening imperfections. A 50-gallon mill requires 200 to 300 pounds of pebbles.

The mill is provided with a large manhole, fitted with a rubber gasket and a cover which can be easily removed, replaced and bolted down. Directly opposite is provided an outlet fitted with a bronze grate and butterfly valve and a screw cap that fits over the threaded end of the outlet. For ease of control of emptying the mill a bronze gate-valve can be fitted to the outlet. A steel plate at this end balances the extra weight of the manhole fittings. A few inches from the top and bottom of the mill, on the side opposite the driving gear, are bored two vent-holes into which brass plugs with threaded ends fit. These are used for sampling and for allowing air to enter during the emptying of the mill.

Pebble mills do not require much power, two 50-gallon outfits being easily handled by a 5-H.P. motor. They are generally driven by tight and loose pulley connection from line shafting, although the small sizes such as the one-gallon experimental mills are driven by direct motor and worm gear, off the lighting circuit.

### Cleaning the Pebble Mill.

Before using, a new ball mill must be thoroughly cleaned and the rough surfaces of the lining and the cement used to join the flint stones together ground smooth. This is done by filling the mill half full of pebbles, adding water till nearly full then bolting on the manhole and running the mill for 4 to 5 hours. Most of the rough projections are ground down to a sludge with the water, which is run off, more water replaced and this continued till the mill has had about twenty hours of running with several successive changes of water. The last batch of liquid should be almost clear. A final washing with water for a few minutes serves to clean off the manhole and gasket and remove most of the grit from the pebbles and outlet valve. The pebbles are then removed and spread on sacking to dry, any broken ones being rejected. The mill is allowed to dry overnight with the manhole open. The lining

of the mill after this treatment should be smooth and clean and after thorough drying the dried pebbles are replaced and the mill is ready for its first charge.

### Charging the Mill.

It is essential for the proper operation of a ball mill that a proper viscosity be chosen for the charge. If too thin, the grinding will be very imperfect and particles of grit from the walls are liable to contaminate the enamel, not to mention the very disagreeable racket and clatter produced by the mill. If too thick, the pebble will not be able to move freely about and thus instead of the succession of many tiny impacts there will be produced a mere heaving of the viscous mass that produces practically no grinding. No one formula will fit all lacquer combinations, for even if the same amount of the same lacquer base were used equal parts of pigment will not thicken up the solution to the same degree. For instance carbon black has a thickening power of several times that of lithopone or ultramarine. It is necessary to determine the proportions to be placed in the mill for each separate formula, and this once determined, to keep the proportions constant thereafter. It is here that control of viscosity of the materials used is important to a high degree.

A useful way to increase the thickness of the batch and at the same time increase the productive capacity of the mill is to grind a pigment stock. This is a solution of cotton and gum containing from 2 to 4 times the percentage of pigment in the finished enamels, which after grinding can be quickly mixed to give that much more enamel for the same time of grinding. Since it takes from 20 to 40 hours to grind a batch properly the value of this procedure is easily seen. The use of a certain amount of high viscosity cotton is advisable, both for the benefit of the grinding and because the pigment stock does not undergo settling of the pigment so rapidly.

In determining the proper proportions for a mixture, the

pigment is first weighed out and placed in the mill, the pyroxylin solution added, and the mill revolved after bolting down the manhole. If after 10 minutes of grinding no sound of the pebbles is heard the mill is stopped with the outlet on top and one or two gallons of thinner added through the valve. The valve is closed, the mill rotated and this continued till the pebbles are just audible, after which the grinding is continued for at least 20 hours. At the end of that time a sample is taken out by inserting a flat strip of tin through the vent-hole and this is spread out on a smooth piece of tile or bristol board and tested for color and fineness of grinding. If still too rough the grinding is continued and samples taken every two hours. The time of grinding is thus established, as well as the proper formula, and thereafter only control of the raw materials is required. The mills are generally run at from 70 to 90 per cent capacity, that is, a mill of rated 50-gallon capacity will be run with from 35 to 45 gallons of liquid. With such pigments as carbon black, it is almost impossible to put the required amount of pigment for 45 gallons of stock, and 35 gallons and sometimes less are run, unless the manufacturer is willing to open the manhole after the mill has run for an hour or so and add the rest of the required pigment.

Even with long and careful grinding the maximum of smoothness is not attained. Grit from the mill and particles of unground pigment are liable to be present and for the finest type of enamel should be removed by straining settling for several days or by centrifuging. The Sharples centrifuge can be adjusted to deliver any required percentage of the enamel, the remaining fraction containing the bulk of the coarser particles being returned to the mill for re-grinding.

It is good policy to have a mill for each important color, generally white, black, blue, yellow and green, although it is possible to get along with one for white, one for black and one for other colors. This can be cleaned out easily by draining the previous enamel, adding 2 gallons of 25 per cent ethyl acetate, 75 per cent benzine solution, turning for a few min-

utes, draining out the cleaning thinner, and repeating once or twice till clean. The thinner can be utilized in subsequent batches of the same color. The manhole and valve should be wiped and rinsed out thoroughly and the mill is ready for another color. The practice of some manufacturers of adding any spoiled blues, greens or browns to the black mill is reprehensible and a mark of improper procedure. The white mill should be kept only for white, as it is very difficult to clean out a colored batch well enough to use for a pure white.

Tints of white are generally made by adding tinting colors ground in castor oil to the finished enamel and mixing either by fastening the cans on a revolving shaft or in a closed paint mixer and then drawing off into cans or drums. Ivories, creams, tans and pinks are thus made without the necessity of keeping on hand more than a small amount of the oil pastes. If a certain color requires more than a few ounces of the paste per gallon this is no longer advisable, as the accompanying oil would soften the film too much. In such cases the color is matched by adding enamels of the proper colors to the white enamels and mixing as before.

In making up the mixture in the pebble mill it should be remembered that the total volume will be that of the liquid plus the pigment and the latter can be calculated from the bulking values given in the table. More than one lacquer chemist with no previous paint experience has added 100 lb. of pigment to 50 gallons of liquid and been pained at the overflow. One hundred pounds of lithopone, for instance, bulks almost 3 gallons, which should be taken in account.

The pebble mill seems almost a necessary part of the lacquer enamel maker's equipment. Even if he uses pastes ground up in oil the best incorporation of such pastes in the lacquer requires a ball mill, as the ordinary paint mixers give a product that is far from ideal. The great advantage of the enamels ground in lacquer is that they lend themselves to plasticizing by the best modern softeners, instead of being restricted to the inferior castor oil. Moreover, where high

bodied enamels are to be made, so much oil is necessarily introduced with the pigment that the product is soft and rubbery. Attempts to avoid this by grinding with a mixture of oil and benzine have not succeeded in giving as well ground a paste. With the pigment stocks ground in lacquer, any conceivable variation of formula can be made, from the hardest to the most pliable enamel, as the plasticizing is the last thing added.

An example in the making of a white enamel will illustrate the practice. The formula called for a pigment stock of 40 gallons, consisting of 150 lb. lithopone, 50 lb. barytes, 3 oz. prussian blue, 25 gal. 16-oz., high viscosity pyroxylin solution, 5 gal. dammar solution and 5 gal. of a thinner consisting of equal parts ethyl acetate and benzol. The pigment was first weighed out and placed in the mill, the dammar solution added, the pyroxylin next and the thinner last. The manhole cover was bolted down and the mill rotated at 38 R.P.M. for 30 hours. The resulting pigment stock contained 3.75 lb. lithopone and 1.25 lb. of barytes per gallon. Twenty gallons were drawn off into five-gallon open mouthed cans, and twenty gallons left in the mill.

The enamel formula called for 50 per cent pigment stock, 20 per cent dammar solution, 25 per cent of 16-oz. lacquer cotton solution and 5 per cent of butyl tartrate. Therefore, to the 20 gallons of pigment stock in the mill, 8 gallons of damar solution, 10 gallons of pyroxylin solution and 2 gallons butyl tartrate were added. The mill was closed, revolved for one hour and then emptied into 5-gallon cans for shipment, after which the first twenty gallons of pigment stock were returned to the mill, the same proportions of dammar, pyroxylin and softener added and the process repeated. By one grinding 80 gallons of a good flat white enamel were produced from a 50-gallon ball mill.

In order to save time some manufacturers add the pyroxylin undissolved, together with the pigments, résins and solvents, to the mill and try to combine grinding, dissolving and

mixing in one operation. The results are bad, for not only is every impurity in the raw material present in the enamel, but during the time required for the pyroxylin to dissolve the pebbles are pelting through a thin liquid which is inadequate for proper grinding and leads to serious erosion of the lining of the mill. The pyroxylin should be separately dissolved and filtered, the resins likewise and the mixture made as described.

Many cheap enamels are made with scrap celluloid or film and the only serious objection to this is that the material generally comes from different sources and the viscosity is scarcely ever the same. Within a certain margin they do very satisfactorily for the purpose and are best dissolved in a rotary eccentric churn such as described for resin-cutting, and the solution used instead of the usual pyroxylin. The solution seldom needs clarification. It must be remembered that the expansion of celluloid is different from that of the 70 per cent pyroxylin, 30 per cent alcohol mixture considered hitherto, as it contains practically no alcohol. The presence of appreciable amounts of camphor, tricesyl phosphate, etc., must also be considered.

### **Ball Mill.**

Some of the largest lacquer makers are now using ball mills instead of pebble mills for grinding. The lining of these mills is steel, and the pebbles are replaced by steel balls. Grinding can be done in much less time in these mills than in pebble mills.

As much heat is generated in the grinding operation, these ball mills are water-jacketed and cooled by a current of cold water flowing through this jacket. In some cases where water-jacketed ball mills were not available, a stream of water was kept playing upon the mill while it was rotating. Ball mills are not suited for white or very light colored enamels, as the steel causes appreciable discoloration.

### The Premier Colloid Mill.

This is the most recent development in the art of grinding and has been experimented with to some extent as a method of grinding pigments. In design it is simple, consisting of a heavy steel base, the stator, carefully hollowed out to a conical center, in which is suspended a heavy rotor also of the shape of a truncated cone which can be adjusted to fit with a few thousandths of an inch clearance of the sides of the stator. The materials to be ground are roughly mixed and forced into the narrow clearance by the rapid rotation, 5000 R.P.M. and more, of the rotor. It is claimed that a combination of shearing, twisting, electrical dispersion and what not takes place in the narrow space and the liquid comes out with the solid in almost ultramicroscopic size and finely disseminated throughout. The capacity of these mills is high, and it is possible that they may be of value in the grinding of pigments in oil. It is doubtful whether it can handle the ordinary lacquers without too much loss but this is being worked on and it may be that a means of eliminating evaporation will be developed.

### Celluloid Rolls.

Some makers use the heated steel rollers with a mixture of pyroxylin pigment and plasticizer to give what is practically a pigmented celluloid which is then dissolved in appropriate solvents to give the enamel. This is probably the most expensive form of grinding.

### Composition of Enamels.

Enamels as a rule employ cheaper and lower boiling solvents than do the metal or wood lacquers. The presence of the pigment slows up the evaporation somewhat and moreover any slight blush would be unnoticed in most colored enamels. This can be pushed too far, however, and such cheap solvents

used that it is difficult for the sprayer to apply a wet uniform coat on a hot day and he thus secures a film speckled with spray dust and of imperfect adhesion. Moreover, the gloss enamels lose much of their luster when a blush settles over them and the black enamels turn grayish. The blacks thus require a higher grade of solvent than the white and other light colors and the gloss enamels need a higher grade than the flat. In any combination of solvents a regular rate of evaporation is essential to avoid streaks, waves and orange-peel.

Adhesion is a most important property of enamels, and a most complicated one. The presence of large amounts of pigment renders the film brittle and of less adhesion to metal or glass than the same lacquer base would possess. Much ingenuity is demanded to secure proper adhesion with minimum cost, and the problem is still only partially solved. The fact that adhesion varies with the type of surface, whether steel, brass, aluminum, wood or glass, and with the method of working the metal make the problem more complicated. Many manufacturers suggest the use of a priming coat such as described in the previous chapter, but this adds considerable additional expense and labor to the job. The ideal condition would be an enamel that would have high coverage, smooth finish and adhesion to any type of material, but at present this is impracticable. The enamels that will do nicely for wood are not so suited for metal, those that will have satisfactory adhesion to brass may not do for tin or aluminum, and while products can be developed for the latter they will be too expensive to compete with those made for the easier surfaces. Aluminum is a difficult metal to finish, even more so than tin which is the paint-maker's touchstone, and requires either a priming coat or two coats of enamel mixed with a lacquer to give the proper effect. Brass is comparatively easy to finish in one coat, and so are steel and iron when previously filled. Wood presents few problems, although there is a tendency for insufficiently plasticised enamels to come away from the edges.

on drying, and the proper filling of the wood is probably the greatest difficulty.

The question of gloss of enamels keeps bobbing up. Some makers turn out both flat and gloss types in their standard colors, others make only a semi-gloss or eggshell finish, recommending a finishing lacquer for increased gloss. The latter seems to be the preferable method, for it not only gives the user a better finish, but it is more economical for the maker who is thus not obligated to keep on hand different glosses of the same color. Some colors such as red and black are in considerable demand as one coat gloss enamels and these are generally made glossy. Very little demand for flat red exists, except as fillers or surfacers while the bulk of the white enamels sold is of the flat or eggshell finish. The demand for black is generally for the flat, rubber and gloss in almost equal proportions with a slight advantage in favor of the rubber black. Most of the other colors are in demand as eggshell finishes, although the toy trade uses quantities of gloss blue and yellow as well as red. The automobile and steel furniture enamels are almost without exception of the eggshell type. Besides the use of a finishing lacquer, an attractive luster can be obtained by polishing or buffing the surface. The last method is used extensively in the finishing of such objects as water-closet seats so as to secure a white, glossy, porcelain-like surface.

For most purposes the flexibility of lacquer enamels is secondary to the hardness, but where the object is to be bent or twisted or subjected to other strains flexibility becomes of great importance and the proper use of plasticisers is one of the most vital points in enamel manufacture. It is more important here than in clear lacquers, as the pigment appreciably increases the brittle nature of the pyroxylin film. Some enamel makers use plasticisers such as tricresyl phosphate in high percentages, employing it to replace some of the resin normally used and thus secure great plasticity and increased resistance to fire. The additional softness given the

film is a counterbalancing disadvantage, however, and the minimum of plasticiser that will meet the situation should be used. Proper plasticisation also enables the enamel to stand such tests as the "hammer test" where an enameled steel plate is struck by a ball-pein hammer so as to make dents of  $\frac{1}{8}$  to  $\frac{1}{4}$  inch depth. A brittle enamel will crack under this test, while a properly flexilized one will follow the contour of the dent without breaking or peeling. It must be remembered in making this test that all enamels grow more brittle with age and that comparisons should be made with enamels applied at approximately the same time. A sharp edged hammer is of no value, as anything can be chipped off a surface by a keen edge forcibly applied.

An excellent test, and one that should be applied to a sample of every batch made, is to thin the sample in a definite manner, one part thinner to two of enamel, or equal parts of each, as the case may be and spray the solution on a standard tin plate. Time of drying, smoothness, gloss, color, coverage and hardness can be examined for by inspection by eye and finger nail while a bending of the plate back and forth will demonstrate whether or not the enamel is properly flexilized. By numbering, dating and filing these plates a permanent record of each batch can be kept in comparatively small space.

For resistance to exposure, particularly in the case of automobile enamels, steel or aluminum plate should be surfaced as the car body would be, the enamel sprayed on, rubbed or sanded exactly as would be done in the finishing of a car, and these plates should then be exposed at an angle of  $45^{\circ}$  and facing the south on a roof or similar open space where sun, wind and rain can do their worst. This test is more rigid than any conditions normally encountered by an automobile, as the car is generally in the garage half the time and thus sheltered from the elements. A surfacer and enamel combination that will stand such a test for 6 to 8 months is generally considered satisfactory.

Pigments settle out of all paints and enamels at a rate

dependent on the specific gravity of the pigment, the size of its particles and the viscosity of the liquid. Instructions on cans of enamel almost invariably include advice to stir or shake well before using, and good sprayers heed this advice. The best type of can for shipping enamels has two openings in the top, one a wide open mouth, provided with a screw top and one a small nozzle opening, generally closed by a cork and pressed tin cap. The can is filled through the wide mouth, which also provides an opening wherein a stirrer can be inserted to mix the contents thoroughly. Drums of enamel can be rolled back and forth to mix the contents, and another method of overcoming the settling is to reverse the position of cans or drums kept in stock every week. This keeps the material more uniformly distributed.

Some users buy enamels in 50-gallon agitator drums, which permit of attaching a crank to the agitator shaft and thus enable the user to stir up the enamel very thoroughly in short time.

Perhaps the best method of shipping and storing enamels is in 5-gallon cans of the type described above. They are somewhat more expensive than the wooden barrels in which some makers transport their material for local delivery, and since they are not returnable really cost more than the lined drums which others use for rail and boat shipments. They are so easily handled, however, that they repay their cost in many cases. Ordinary iron or steel drums can be used for dark enamels but for whites and light tints the tin or white metal-lined drums are preferable. A type of tin or terne-plate lined 5-gallon pail is now in use for shipping lacquer enamels. It has a specially devised top that permits of closing the pail tightly enough to conform with the I. C. C. regulations and is of sturdy enough construction to permit of shipment without the wooden case and packing required for tin cans. These pails permit of an appreciable economy in package and freight cost.

Enamels are generally applied by spraying and the pro-

cedure is described in more detail in the following chapter. Some articles which have a uniform shape, such as ornamental candles, pencils, broom and brush handles, etc., are often dipped. This procedure is also described later, and is the most economical for such objects. A dipping enamel must be made of a viscosity and rate of drying that allow a smooth film with minimum drip and great uniformity to form around the object. Too thin a liquid will run off and leave bare spots, too thick a one will harden in a gob except when a gasket is used. The dipping baths are usually open and as the volatile solvents go off the bath becomes thicker and must be thinned to the proper viscosity at regular intervals to secure the best results.

The following formulas typify the important varieties of enamels made with a pyroxylin base. It should be understood that these formulas are merely the final proportions, but that the dissolving of the separate ingredients and the grinding of the pigments are done as described earlier. Satisfactory enamel will not be made by merely mixing all the ingredients in a mill and allowing to grind.

#### WHITE ENAMELS

1	2
Egg Shell White (high grade)	Egg Shell White (cheap)
1½ lb. zinc oxide-white seal	¼ lb. silica
¾ lb. titanox	½ lb. zinc oxide
4 oz. high viscosity pyroxylin	1½ lb. lithopone (light-proof)
18 oz. ½ sec. pyroxylin	8 oz. high viscosity pyroxylin
2 pts. dammar solution	4 oz. ½ sec. pyroxylin
2 pts. butyl acetate	½ pt. dammar solution
1 pt. butanol	½ pt. ester gum solution (8 lb.)
3 pts. toluol	½ pt. light acetone oil
8 oz. tricesyl phosphate	1 pt. methyl acetone
	½ pt. ethyl acetate
	1 pt. denatured alcohol
	3 pts. benzol
	6 oz. castor oil

3

White Enamel for Tin, Aluminum  
Glass

1/8 lb. silica
3/4 lb. zinc oxide
1/2 lb. titanox
4 oz. H. V. pyroxylin
20 oz. 1/2 sec. pyroxylin
1/2 pt. dammar solution
1/2 pt. shellac solution
1 pt. ethyl acetate
1 pt. butyl acetate
1/2 pt. butanol
2 1/2 pts. toluol
1 pt. benzol
8 oz. dibutyl phthalate

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4

## Dip Gloss White Enamel

4 oz. whiting
3/4 lb. titanox
1/2 lb. zinc oxide
6 oz. H. V. pyroxylin
8 oz. 1/2 sec. pyroxylin
1/2 pt. ethyl acetate
1/2 pt. butyl acetate
1/2 pt. butyl propionate
1 1/2 pts. butanol
3 pts. dammar solution
2 pts. toluol
6 oz. dibutyl phthalate

---

5

## Sprayed Gloss White

1 lb. titanox
1/4 lb. zinc oxide
4 oz. H. V. pyroxylin
8 oz. 1/2 sec. pyroxylin
3 pts. dammar solution
1 pt. butyl acetate
1 pt. butanol
3 pts. toluol
6 oz. dibutyl phthalate

---

6

## Cheap Gloss White

1 lb. lithopone
1/2 lb. titanox
10 oz. scrap celluloid or film
2 pt. dammar solution
1 pt. ester gum solution
1 pt. ethyl acetate
1/2 pt. light acetone oil
1 pt. denatured alcohol
2 pts. benzol
1/2 pt. solvent naphtha
5 oz. castor oil

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N.B. Formulae 2 and 6 are liable to be yellowish, and this is overcome by adding about 1 oz. prussian blue or ultramarine blue per 30 pounds of pigment.

**BLACK ENAMELS****Flat Black Enamel—Pigment Stock.**

Prepare a solution of 8 oz. medium viscosity pyroxylin per gallon of solvent, made up of ethyl acetate  $1\frac{1}{2}$  pts., butyl acetate  $1\frac{1}{2}$  pt., butanol  $\frac{1}{2}$  pt., denatured alcohol  $\frac{1}{2}$  pt., benzol 2 pts., toluol 2 pts. Grind 8 oz. of high grade carbon black and 2 oz. lamp black to each gallon of the solution, for 36 hours in a ball mill. If the mixture is too thick, thin with methyl acetone till the pebbles are just audible.

**Flat Black Enamel**

$1\frac{3}{4}$ pts. pigment stock
$\frac{1}{2}$ pt. ester gum solution (6 lb. cut)
4 pts. 16 oz. lacquer cotton cut in above solvents
$\frac{1}{2}$ pt. butyl acetate
$\frac{1}{2}$ pt. acetone
$\frac{3}{4}$ pt. tricresyl phosphate

**Rubber Black Enamel**

$1\frac{1}{2}$ pts. pigment stock
$1\frac{1}{2}$ pts. ester gum solution
$3\frac{1}{2}$ pts. 16 oz. lacquer cotton
1 pt. butyl acetate
$\frac{1}{2}$ pt. tricresyl phosphate

**Gloss Black Enamel**

Dissolve 4 pounds gilsonite to 1 gal. benzol. Filter.

Dissolve 1 pound spirit soluble nigrosine in 1.5 gals. denatured or wood alcohol. Filter.

Make a 16 oz. solution of lacquer pyroxylin in the solvents used for the flat black.

**Gloss Black**

$\frac{1}{2}$ pt. gilsonite solution
$1\frac{1}{2}$ pts. dammar solution
4 pts. lacquer solution
$1\frac{1}{4}$ pts. nigrosine solution
$\frac{1}{2}$ pt. butyl acetate
$\frac{1}{4}$ pt. dibutyl phthalate

Black enamels of varying degrees of gloss can be obtained by mixing the flat and gloss enamels in different proportions.

### GRAY ENAMELS

These can be made by mixing white and black in varying proportions, or by adding lampblack or bone black ground in castor or linseed oil to a white enamel of the proper characteristics. A small amount of black is generally sufficient. Grays of the blue-gray and green-gray types will be discussed later. A dove gray can be made by adding 4 parts of ultramarine and one of bone black to 50 parts of white. The description and the matching of grays are vexing problems, and a good eye and skill in recognizing the colors present are required.

### RED ENAMELS

High Grade Gloss Red Enamel (Pigment stock)	Enamel
1½ pts. toluidine red	2 pts. pigment stock
8 oz. high viscosity pyroxylin	2 pts. 16 oz. lacquer cotton solution
1 pt. ester gum solution	1 pt. 32 oz. ½ sec. cotton solution
1 pt. ethyl acetate	½ pt. butanol
1 pt. butyl acetate	½ pt. tricresyl phosphate
½ pt. butanol	
1½ pts. benzol	
3 pts. toluol	
Grind 24-30 hours.	

#### Maroon Enamels (high grade)

¾ lb. venetian red		2 lbs. of a maroon lake may be substituted
½ lb. para toner		
¾ lb. prussian blue		
4 oz. H. V. pyroxylin		
24 oz. ½ sec. pyroxylin		
2 pts. dammar solution		
2 pts. butyl acetate		
1 pt. butanol		
3 pts. toluol		
10 oz. dibutyl phthalate		

Pinks, corals, flesh colors, etc., are generally made by tinting a white with toluidine, tuscan and Indian reds ground in castor or linseed oil.

### BLUE ENAMELS

#### Light Blue Enamel (egg shell)

$\frac{1}{2}$  lb. lithopone  
 $\frac{1}{2}$  lb. blue ultramarine  
6 oz. H. V. pyroxylin  
10 oz.  $\frac{1}{2}$  sec. pyroxylin  
1½ pts. ester gum solution  
1 pt. ethyl acetate  
1 pt. butyl acetate  
1 pt. butanol  
1 pt. benzol  
2½ pts. toluol  
8 oz. tricresyl phosphate

#### Dark Blue Enamel

Substitute 2 oz. lampblack for the lithopone.

#### Marine blue

4 oz. ultramarine blue  
2 oz. carbon black  
Substitute these for the pigments in the formula for light blue enamel.

#### Delft Blue

1¼ lb. cobalt blue  
1 oz. lampblack  
Substitute as above.

#### Blue Gray

7½ parts white enamel  
2 parts light blue enamel  
½ part flat black enamel

#### Robin's Egg Blue

100 parts white enamel  
16 parts ultramarine blue enamel  
10 parts chrome green enamel

#### Turquoise Blue

White enamel with 3 oz. ultramarine blue and 1 oz. chrome green in oil per gallon.

#### Baby Blue

100 parts white enamel tinted to shade with prussian blue and chrome yellow in castor oil. 4 parts blue and 1 part yellow are generally used.

## GREEN ENAMELS

Green Auto Enamel

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1 $\frac{3}{4}$ lb. chrome green
$\frac{1}{4}$ lb. lemon chrome yellow
4 oz. lampblack
4 oz. H. V. pyroxylin
24 oz. $\frac{1}{2}$ sec. pyroxylin
1 $\frac{1}{2}$ pts. dammar solution
1 pt. amyl acetate
1 pt. butyl acetate
1 $\frac{1}{2}$ pts. butanol
2 pts. toluol
12 oz. dibutyl phthalate

---

1.17 gallons enamel

## Olive Green (auto enamel)

Use  $\frac{1}{2}$  lb. burnt umber  
1 lb. chrome green  
 $\frac{1}{4}$  lb. lemon chrome yellow

or

$\frac{1}{2}$  lb. French ochre  
 $\frac{1}{2}$  lb. ultramarine blue  
 $\frac{3}{4}$  lb. burnt umber  
 $\frac{1}{4}$  lb. lithopone

Cheap Gloss (green enamel)

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1 lb. chrome green
$\frac{1}{4}$ lb. titanox
6 oz. H. V. pyroxylin
4 oz. laquer pyroxylin
2 pts. ester gum solution
$\frac{1}{2}$ pt. butyl acetate
$\frac{1}{2}$ pt. butanol
1 pt. ethyl acetate
$\frac{1}{2}$ pt. denatured alcohol
2 pts. benzine
1 pt. toluol
8 oz. tricresyl phosphate

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1.07 gallons enamel

## Apple Green

Use 1 $\frac{1}{2}$  lb. zinc oxide  
1 oz. chrome green

## Pistachio Green

White enamel tinted with bone-black, French ochre and chrome yellow in oil.

## Gray Green

Add 1 oz. bone-black and 2 oz. chrome green in oil to 1 gallon white enamel.

## BROWN ENAMELS

The formulae for these, and in fact any colored enamels, can be based on the previously given variety of formulae, with the necessary changes in pigment.

For seal brown use 4 parts burnt umber to 1 part ochre.

For chestnut brown, 1 part umber, 4 parts medium chrome yellow, 1 part venetian red.

For olive brown, 3 parts burnt umber, 1 part lemon chrome yellow.

For tan, 20 parts lithopone, 6 parts umber, 1 part ochre.

### BRUSHING LACQUER ENAMELS

One of the most remarkable accomplishments of lacquer chemists has been the formulation of lacquer enamels which permit of reasonably successful application by brushing, even in the hands of inexperienced users. Of course, lacquers are still more difficult to brush than paints or oil enamels, but on small work such as shelves, chairs, toys, etc., very good results can be obtained with several of the brands of brushing lacquer now on the market.

There were several stumbling blocks in the way of formulating these lacquers. First of all, the lacquer had to be brushable, that is, it had to possess a flowing quality that permitted the user to brush, cross-brush and lap without leaving ridges or brush-marks. The use of alcohols, notably butanol, ansol and hexalin, together with the higher esters such as butyl propionate, combined with low-viscosity pyroxylin, a high percentage of resin, and such plasticisers as lindol, dibutyl, phthalate and castor oil has enabled this to be achieved with reasonable success. Some brushing lacquers contain high proportions of treated linseed or perilla oils, generally with the addition of cobalt or lead-manganese driers.

The second requirement was that of being as inert as possible to the first coat whether that be lacquer or previously applied paint or varnish. This meant the reduction of active solvent to an absolute minimum, a high percentage of alcohols as discussed above, and the substitution of benzol and toluol in great measure by petroleum hydrocarbons akin to gasoline. Even to-day this problem is but incompletely solved,

as some kinds of varnish, particularly the short oil tung oil type, are liable to be acted on by lacquers to give a very ugly wrinkled and blistered surface. Whether it will be possible to work out a solvent combination that will dissolve pyroxylin and resins and yet not attack any previous finish is doubtful, to say the least.

The coverage of brushing lacquers is about one-half that of good oil enamels. Even this is obtained only by using colors of highest opacity and tinting strength, such as titanox and high-strength lithopones, for white, pure toners for red, C. P. greens, etc. The lustre is variable, depending on the brand and color—generally being about an eggshell sheen.

### Crackle Enamels.

Many objects of varied nature, notably radio horns and battery eliminators, furniture, etc., have been finished with crackle lacquer enamels. These are lacquer enamels in which the pigment content is too great to be kept together by the lacquer binder, so that when they are sprayed on a lacquer ground coat they split apart in irregular cracks, which show the color of the ground coat. The heavier the coat of crackle and the closer the gun is held to the work, the larger will be the crack, which can be made so small as to be barely visible by just fogging on the crackle. While these lacquers have no adhesion to speak of, there is enough softening and amalgamating caused by the solvents to attach the crackle firmly to the undercoat. The crackle surface is often given a protective coat or two of either gloss or flat clear lacquer. By proper manipulation leather effects can be obtained, furniture can be made to have the effect of paint cracked by age, and various odd and agreeable finishes secured. By using the proper transparent pigments a clear crackle can be obtained, which resembles when applied a varnish coat cracked and checked by age.

### FILLERS

To secure a smooth finish with lacquer enamels on rough or porous surfaces such as wood or cast iron it is almost always necessary to use a filler. This is of great importance in the furniture and automobile trades, in the first because it would otherwise require too many coats of enamels to give a smooth surface on the wood, and in the second because of the necessity of filling the file and hammer marks on the bodies of the cars.

The purpose of fillers is to fill, and consequently they contain as much pigment as possible. This makes them brittle and they should always be protected by a finishing coat of enamel. On material subject to bending and twisting they are to be avoided and the effect secured by spraying cheap enamel undercoats. Fillers generally come in white, black and slate gray colors to be used under the corresponding enamels.

In formulating a filler it is obvious that the cheapest pigments are to be sought and they are such materials as silica, barytes, lithopone, whiting, bone black, umber and ground slate. Opacity is a secondary consideration, as the covering is really obtained by the top coat or coats of enamel. Gloss is also of no moment, although certain amounts of resin are used to cheapen the product by replacing some of the pyroxylin. With the excellent oil fillers and undercoatings on the market, the pyroxylin undercoatings hold their place primarily because of the fact that the pyroxylin enamels give better results with their own type of filler and undercoatings, sometimes called surfacers, rough stuffs or flat primers. Their speed of drying also gives them some advantage over the much cheaper and more highly bodied competitors. Until recently much trouble was experienced by automobile finishers using the lacquer finishes because of incompatibility between the oil undercoats and the pyroxylin enamels. This has now been overcome by properly formulated red oxide and

similar primers which when thoroughly dried serve splendidly as a base for pyroxylin. Certain of the large lacquer makers have now developed finishing systems whereby only pyroxylin primers, fillers, glazes and enamels are used, and although they have not been out long enough for a definite statement of their quality, it is reasonable to believe that most of the lifting peeling and checking of lacquer finishes will be thus eventually eliminated.

Knifing glazes are fillers of very high solid content and of a pasty consistency, which are used to fill comparatively deep dents and scratches. These are generally so thick that they cannot be ground in a ball mill, and are best made by mixing a paste of pigment in castor oil with the lacquer in a roller mill or a closed paint mixer provided with a powerful stirrer and a wide outlet. A putty mixer with a tight fitting cover serves nicely for the purpose. Knifing glazes require high boiling solvents, as otherwise the material would dry too rapidly for the putty knife to remove the excess.

### KNIFING GLAZES

#### **White Knifing Glaze.**

Make a paste of 50 lb. lithopone, 40 lb. whiting, 10 lb. silica with 15 lb. castor oil and 15 lb. solvent naphtha. The three-roll mill is best for the purpose. Make a solution of 32 oz.  $\frac{1}{2}$  second cotton in a gallon of solvent consisting of 10 per cent acetone, 25 per cent butyl propionate, 10 per cent butanol and 55 per cent xylol or solvent naphtha. To each gallon of pyroxylin solution add 12 pounds of paste and mix thoroughly.

#### **Gray Knifing Glaze.**

Same as above, but with 100 pounds of ground slate as pigment.

**Black Knifing Glaze.**

Same as above, but with 20 lb. bone black, 40 lb. whiting, 20 lb. silica.

**WOOD FILLERS AND UNDERCOATS****White Wood Undercoat**

1 lb. whiting	
1 lb. lithopone	
$\frac{1}{2}$ lb. silica	
$\frac{1}{2}$ lb. talc or asbestos	
24 oz. $\frac{1}{2}$ sec. pyroxylin	
2 pts. methyl acetone	
$\frac{1}{2}$ pt. acetone oil	
1 pt. ethyl acetate	
1 pt. denatured alcohol	
3 pts. benzol	
8 oz. boiled linseed oil	
<hr/>	
1.15 gallons	

**Black Wood Undercoat**

1 lb. barytes	
1 lb. whiting	
$\frac{1}{2}$ oz. bone-black	
2 oz. carbon black	
in the same solution as the white wood filler	
<b>Transparent Filler</b>	
(For Wood)	
2 lbs. silica	
1 lb. whiting	
$\frac{1}{4}$ lb. barytes	

These fillers are often tinted with small amounts of umber, ochre, venetian red, etc., so as more nearly to approach the color of the desired wood finish. Since the fillers are transparent, small amounts of tinting colors suffice.

Some furniture makers use a heavy bodied flat enamel to act both as filler and first coat or primer for the enamel that follows. On close grained wood such as birch this is adequate, and one coat of a flat white followed by one or two of the egg-shell enamel gives an excellent finish. If the cheap enamels used by the lighting fixture and metal toy trades be employed, it will be found necessary to use more coats. A top coat of finishing lacquer will give a better and glossier finish.

**METAL FILLERS**

These are used to fill file-marks, scratches and shallow depressions. For deeper blemishes the knifing glazes are

employed. Metal fillers as a rule do not require the body of a wood filler, but do demand more adhesion and flexibility. The perfect filler is still to be found, but the following have met with some success on an experimental scale.

#### White Filler

2 lb. lithopone  
 $\frac{1}{2}$  lb. silica  
 4 oz. H. V. pyroxylin  
 18 oz.  $\frac{1}{2}$  sec. pyroxylin  
 1 pt. ester gum solution (8 in. cut)  
 1 pt. ethyl acetate  
 $\frac{1}{2}$  pt. methyl acetone  
 $\frac{1}{2}$  pt. acetone oil  
 1 pt. denatured alcohol  
 3 pts. benzol  
 9 oz. tricresyl phosphate

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1.10 gallons

#### Gray Filler

Same as white with  $1\frac{3}{4}$  lb. of finely ground (200 mesh) slate and  $\frac{1}{4}$  lb. talc as pigments.

#### Black Filler

Same as white, using  $1\frac{3}{4}$  lb. bone black and  $\frac{1}{2}$  lb. silica as pigment. The ester gum can be replaced partially by gilsonite in benzol.

Fillers are invariably more brittle and less durable than enamels, which have a smaller ratio of pigment to binder. Where it is possible to afford it more coats of enamel should be used instead of a filler, as the latter to some extent renders the succeeding coats of enamel less durable and more brittle. There are cases, however, where fillers must be employed, particularly on iron castings and automobile bodies which are deeply file marked and dented, and where the trade demands a perfectly smooth finish. Where time permits, the oil primers and fillers seem best adapted for the purpose at present.

With the great interest now being displayed in lacquer enamels and under coatings and the activity in research that this is caused, it is safe to assume that even better products than the present ones will soon be forthcoming. The proper blend of pigment, pyroxylin gum and plasticiser to give the best results will eventually be found by patient and careful experiment. But even to-day it can be confidently claimed that a high-grade pyroxylin enamel affords the best finish

procurable, with the possible exception of the vitreous enamels which belong to an entirely different category and are out of the question for most purposes. These vitreous enamels are practically opaque glasses of low melting point and are baked on at fairly high temperatures. Such materials as ranges, bathtubs, cooking utensils, etc., are best finished with this type of enamel, which is waterproof, fire-proof and light-proof, although very brittle and easily fractured by a blow or fall.

### Matching of Colors.

Accurate and speedy matching of colors is an art acquired only by long experience. Not only must the actual color be considered, but its depth, the gloss of the enamel, the length of time it had been applied and whether or not a clear finishing varnish or lacquer had been applied. Two colors that match according to the eye in the liquid state will dry to quite different hues; a sprayed enamel gives a different shade from the same enamel poured or brushed. Probably the best method for a manufacturer who has no color expert is to have a chemist make up different combinations of primary color enamels, spray or flow samples on bristol-board with the date and composition, and, after drying, cover half of each sample with a finishing lacquer. If 100 or so representative combinations are made it should be possible to pick out a close approximation to any sample submitted and start work from that basis if a more exact match is desired. For accurate duplication of a special color most manufacturers insist on a ten or twenty gallon minimum order, as smaller samples will be more subject to errors in weighing or measuring and thus, when a large batch is made it is liable to be off color. The vagaries of purchasers in regard to shade of color are the cause of much loss of time and labor in paint, varnish and lacquer houses—one large manufacturer with nearly 1500 standardized shades on record being frequently requested

to make a color between two closely similar shades, while almost every one in the trade meets the request to make up something like No. 234-X but with a little more red or a little less blue, etc. A color that often irritates the production men is olive-green, which name covers perhaps a dozen or more shades ranging from a greenish-brown to a dark, almost bottle-green. Some standardization of color names, so that a name will mean a definite pigment proportion or standard tintometer glass would be a great boon to all those in the paint and allied industries.

In matching a color it is best to start with about half of the required amount. By the time the various tinters have been added and their excess counterbalanced by the addition of the basic shade the volume of the mixture is generally doubled. A good north light should be used for matching colors, with the so-called "daylight" electric light as second best. The latter is produced by a special glass that allows a mixture of light rays that closely approximates daylight to pass through the bulb and is widely used in microscopic and other work where this is required. A white tile or porcelain palette is of great value for matching colors as well as for the examination of pigments and should be part of the equipment of the enamel room or laboratory.

If an enamel is to be sprayed, the final matching should be done with a sample thinned to the proper degree and sprayed on a surface as nearly as possible the same as the original sample. If the original sample is a liquid, it may be applied to one half of a small glass slide and the matched material applied to the other half. After drying, any difference between the two can readily be seen by holding the glass to the light and looking through it from the reverse side.

## CHAPTER XI

### APPLICATION OF PYROXYLIN SOLUTIONS

Until 1910 or thereabouts lacquers were either brushed or dipped. The brushing lacquers were applied with a soft camel's-hair brush and were made of a rather high body and with high-boiling solvents, chiefly amyl acetate and fusel oil, as the more volatile solvents would dry too quickly on the brush. Brushing had to be done rapidly and generally with one sweep of the brush, as criss-crossing would leave brush marks in the rapidly drying film. Brushing was, of course, slow and cumbersome and dipping was soon adopted as the standard method.

The dipping tanks were made either of wood or of tin and where enamels were used, were provided with agitators to keep the pigment uniformly suspended. Much ingenuity was displayed in the devising of wire cages and hooks for handling the objects to be dipped, one of the best for some classes of work being a type of tumbling barrel wherein the articles were placed together with the lacquer. The barrel was centered on a shaft inclined obliquely to the horizontal and the objects placed in an inner cylinder of wire cloth. After turning for a few minutes the excess lacquer was allowed to drain off, the wire container removed and the film allowed to dry either in the air or in a steam heated drying-room.

Dipping lacquers were thinned as far as possible, as the object was to secure a protective film of minimum thickness. If iridescence was found present on the finished article, the dipping was repeated.

In all cases careful cleaning of the metal was found neces-

sary. It was first given a dip in alkali, dried, plunged quickly into dilute acid and then into hot water, dried again, brushed or burnished and lacquered as quickly as possible to avoid tarnishing by air. The lacquering rooms of the better class were dust free and not subject to strong air currents. The plated articles were sometimes taken directly from the plating bath and dipped into a lacquer which contained water-insoluble solvents, such as amyl acetate and benzine. The theory was that the adhering water would drip off the metal and collect in the bottom of the tank, but it was very difficult to secure really adherent coats of lacquer on surfaces in this manner. Moreover a rapid and expensive contamination of the lacquer was observed that generally outweighed the cost of cleaning the object. On cheap work the water dip lacquers are still used, but they are now generally copal or ester gum solutions containing no pyroxylin.

The fire risk from open tanks of lacquer is naturally considerable and was one of the reasons for the rapid increase of favor obtained by the spray gun. Another was the frequent contamination by dust, grease or other dirt of a dipping tank full of expensive lacquer and a third was the loss by evaporation during the day's work. Dipping is now seldom used except for very small articles made in great quantity, and as previously mentioned for cylindrical objects of small diameter such as lead pencils and broom handles.

These are generally handled by machinery, a gross or more being fixed in sockets on a frame that is lowered in and out of the dipping tank by a manually operated handle or by a falling weight. Motor driven outfits operating through gears are also used and give the most uniform results. The viscosity of the dipping bath is adjusted according to the dimensions of the objects to be dipped, the frame holding the articles is lowered into the bath, withdrawn at a rate approximately 6 inches per minute, the frame removed and placed in a drying room and another one placed in the dipping bath.

An interesting development is the so-called gasket dip,

used largely for broom handles, vacuum cleaner handles, etc. The handle is dipped into the liquid, which is very viscous, and withdrawn through a close fitting gasket of pure rubber which sweeps off excess lacquer or enamel and leaves a film of uniform thickness. The gaskets are attacked by most lacquer solvents and must be replaced at frequent intervals.

In the brass spinning and copper plating industries a variety of finishes were developed by the action of certain chemicals on the copper or copper-plated brass followed by lacquering. Most of these have been superseded at present by lacquer enamels and by the use of the numerous varieties of bronzing powders suspended in bronzing liquids. They are still occasionally used and may be mentioned.

The so-called statuary bronze effect was gained by dipping the copper surface into a dilute solution of potassium sulfide ( $\frac{1}{4}$  oz. per gallon of water) for a few seconds, scratch-brushing the surface after drying, and then lacquering. Ammonium sulfide was sometimes used and gave a slightly greener bronze.

The Tiffany green finish was obtained by first dipping in a solution containing  $\frac{1}{2}$  lb. copper sulfate and  $\frac{1}{2}$  lb. of ammonium chloride to a gallon, drying, and then dipping in or stippling with a solution of 8 oz. copper sulfate, 12 oz. ammonium chloride, 4 oz. salt, 1 oz. zinc chloride, 1 oz. glycerine and  $1\frac{1}{2}$  oz. acetic acid. After drying the high lights are brushed with beeswax and a very pretty finish is obtained.

Much trouble encountered by platers in the use of lacquer has been due to inadequate cleaning and to errors in plating. A poorly deposited nickel or copper plate may peel off and carry the lacquer with it and a common tendency of the plater was and probably is to blame the lacquer for it.

A black finish on copper can be obtained by dipping in copper nitrate solution, heating, brushing, and lacquering. This is now being almost entirely superseded by the black enamels which are now adhesive, durable and hard enough to give satisfactory service and are easily applied. Black enamels are also supplanting the Bower-Barff method of treating

iron objects, namely by heating in an oxidizing atmosphere at a high temperature, thus forming a scale of black magnetite about the iron.

The advent of the spray gun has revolutionized the art of finishing, and although used largely with paints and varnishes it is of particular importance with the present-day lacquers and enamels. The use of economical and highly volatile solvents has made brushing in great measure impracticable and the necessary thicknesses of film are with difficulty given in a one coat dip. The spray gun permits of the use of almost any formula and the deposition of a film of the requisite thickness in a minimum of time and with the maximum of accuracy. There is no wastage of large batches due to accidental contamination, and with a properly constructed spray chamber there is no more and probably less fire risk. By the use of different types of available spray guns and nozzles a spray jet can be projected that is only of pencil-like diameter or a fan shaped jet covering more than a square foot can be played on large surfaces such as automobiles, walls, cabinets, etc., with any desired intermediate size.

The spray gun is essentially an atomizer similar to the familiar perfume and medicine atomizers. A blast of compressed air sweeping over a nozzle creates a suction in the nozzle that draws up the liquid which is then broken up into a fine spray by the stream of air and carried by it to the desired point. This is the simplest type and is illustrated in such an apparatus as the Eureka sprayer. The latter is a pistol-shaped handle provided with a tapered screw thread for the air hose and a narrow opening through which the air blows. At right angles to the air hole a tube dipping into a glass jar containing the lacquer and provided with a series of nozzles of different diameters which are used for different viscosities and different diameters of spray jets. The smallest nozzle can only be used for thin liquids and gives a rather narrow jet. The widest is used for quite viscous liquids such as heavy enamels and stippling compositions and gives a wide,

coarse spray. The jar for holding the lacquer is generally a one-pint mason jar and a dozen or more are usually purchased with the set. By using each jar for a different color the annoying cleaning out of the gun is reduced to a minimum, as only the tube and nozzle need be cleaned. For polychrome and similar art work a model is made with two or three different tubes and nozzles on the same instrument, and this saves time where it is desired to spray different colors on an object.

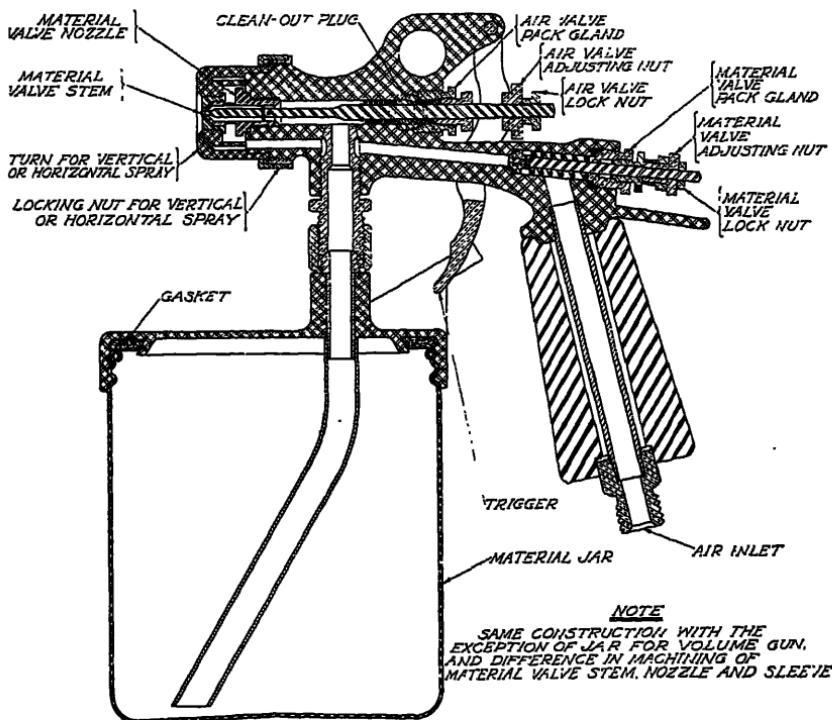


FIG. 12B—Matthews Spray Gun.

In spraying with any type of gun there are a few simple rules to follow. The work should be clean, and not too hot or too cold. The size of nozzle and the pressure should be adjusted to the nature of the lacquer and of the type of work to be done. Spraying should be done at an angle of 45 degrees

to the work, which is best mounted on a rotating, tilting turn-table. The gun should be held at a distance of 5 to 10 inches from the work, depending on the volatility of the solvents and on the pressure used. The sprayer should always keep a wet surface on the work, although too close spraying or using too wide a nozzle will give a coating that it too wet and sags or runs. The general procedure on flat, stationary work is to start at the upper left-hand corner, sweep horizontally across, lower the gun a few inches and sweep back from right to left and repeat till the whole surface has been covered horizontally. Many sprayers follow this by spraying vertically, again starting at the upper left-hand corner. When finishing objects with broken contours such as chairs, tables, etc., a gun with an adjustable nozzle is almost necessary for economical work, as the narrow arms and legs require a narrower spray than the seats and tops to avoid loss of lacquer, while on the other hand the latter require a wide spray for economy in time.

When work is to be done with one color at a time on a large number of pieces, it becomes too cumbersome to use the small jars that require frequent refilling. The Binks, Paasche and de Vilbiss spray guns are so arranged that quantities up to 5 gallons of lacquer can be placed in a container that is suspended over head and communicates by a hose to the nozzle. By varying the pressure on the trigger different rates of flow of the material through the nozzle are obtained. These guns are very helpful on large scale, one-color work and improvements are constantly being made. Lacquer manufacturers often have complaints from users whom they have converted from paints and varnishes, due to neglect on the latter's part to realize the different volatilities and viscosities of the lacquers. Some common errors are: holding the gun too far away, thus securing a powdery effect due to spray dust; using too wide a nozzle, which often causes blobs of enamel to spurt over the finish; and such occasional lapses as turning on the heater used to reduce the viscosity of paints while spraying with lacquer.

Bronzing liquids, as previously described should be mixed with the bronze or aluminum powder just before spraying in order to avoid the greening and gelatinizing of the solution. While a good bronzing liquid should adhere well and give a good finish on most metals in one coat, on wood, reed and other porous material it is generally the custom to fill the wood with an oil, water or pyroxylin filler in order to avoid wastage of the expensive bronze powder through absorption by the porous material.

Since the spray of paints and lacquers is very inflammable as well as disagreeable, spray hoods are provided with means for ventilation. The hoods themselves are generally made of galvanized iron, and contain a platform of convenient height for the work to be done therein and usually a turn-table, preferably of the motor-driven, tilting type. An electric light bulb, protected by a safety guard is very desirable, but special care must be taken that no short circuits or sparking can occur. The ventilation is either up-draft or down-draft and is provided for by a galvanized iron tube or chimney leading out to the open air. In the up-draft type, the opening of the chimney is about on a level with the turn-table and usually leads out through a window pane to the outside air. A revolving fan driven by a  $\frac{1}{4}$ -H.P. motor of the induction or other non-sparking type serves to draw out the fumes while an adjustable slide or damper is of value in preventing the entry of rain, cold air, or such not uncommon missiles as lighted matches, cigarettes or fire works from mischievous children when the spray apparatus is not in use. The down-draft type is similar, but is so arranged that the sprayed articles are on a wire screen resting on the chimney with the result that the vapors are drawn down by the fan and ejected at some point underneath. Since the fumes are heavier than air, this seems to be the more logical type, but the up-draft is more commonly used.

An advantage of lacquers over paints and varnishes in this connection is that the fumes of the former are either vapor or

solid and easily removed, while in spray hoods using the latter materials regular overhauling and cleaning of the fan-blades from the oily accumulation is necessary.

A type of double spray-hood has the two units joined back-to-back and one ventilating system serves for both with economy in initial cost and in power. The air compressors and other accessories are of numerous types and no particular standard can be set. It is, of course, essential that the air compressor be of sufficient capacity to meet any peak loads in spraying, and that the air reservoir be of strong construction to avoid the possibility of explosion. Since modern automobile spraying is conducted at a pressure often exceeding 100 lbs. per square inch, a cheap un-inspected tank is a menace. A very useful, in fact almost necessary device is a pressure regulator with automatic cut-off so arranged that when the desired pressure is reached the motor is stopped, to start again when the pressure drops below the required point. This permits of regular and even spraying without the trouble and spoilages incident to a hand operated control. Another very useful adjunct is an oil and water separator and air filter. As the outside air is compressed, the excess moisture is liable to be precipitated out and this, together with oil from the compressor or dust from the air might spoil a delicate spraying job.

Portable spraying outfits are available which can be connected to the electric light fixtures or in some cases to an automobile truck motor. They are much used by interior decorators and by men who spray bathroom fixtures. They are generally only suited for comparatively low pressures, 20 to 40 lbs. per square inch, but this is sufficient for their purposes. Since the expense of an air compressor and its accessories is rather high, attempts have been made to adapt the common, cheap and readily accessible cylinders of carbon dioxide to the purpose. Results have not been very satisfactory thus far, primarily because of the chilling of the spray by the cold expanding gas. If the difficulties are overcome,

and small cylinders of this gas procurable at a reasonable price, the field of lacquer and lacquer enamels may be extended to cover a large percentage of the handy householders who could decorate his home and furniture, and possibly his car with the easily applied, quick drying and durable lacquer finishes.

Recently compressed nitrogen has been put on the market in tanks of 200 cubic feet capacity which allow more than half an hour's continuous use at the average rate of 6 cubic feet per minute. Being both incombustible and a non-supporter of combustion, nitrogen has marked advantages over compressed air and oxygen or hydrogen. Its chilling tendency on expansion is notably less than carbon dioxide. For small plants, refinishing shops and contractors' equipment, where only occasional spraying is to done, the use of compressed gas as a source of pressure has promise.

The standard manufacturers of spray guns and allied apparatus will gladly furnish complete descriptions and instructions for operation of their products and such information can be secured from de Vilbiss Manufacturing Company, Toledo, O.; Paasche Air-brush Co., Chicago, Ill., Eureka Manufacturing Company, Richmond Hill, N. Y., Binks Spray Equipment Co., Chicago, Ill., W. N. Matthews Co., St. Louis, Mo., and Willard Beach Co., Harrison, N. J., etc.

The pressure to be used in spraying depends on the material sprayed. For bronzing liquids, clear metal lacquers, etc., of a low viscosity 30 to 40 lbs. pressure is generally used. For ordinary enamels 35 to 65 lbs. is the customary pressure but it is stated by spray foremen who are handling automobile finishing by this method that pressures from 90 to 120 lbs. are used with the result that the so-called orange peel effect is greatly diminished and a smoother surface obtained. Enamels to be used at these pressures should predominate in high boiling solvents, as the more volatile ones would form too much spray dust under the conditions. For some decorative effects, such as stippled bronze, a very low pres-

sure (15 to 20 lbs.) and a wide nozzle are used. The bronze is thus ejected in coarse drops which are not atomized by the air and are deposited as isolated patches rather than a continuous film.

The spray room should be dust-free as far as possible and should be kept clean. Spray guns and jars should be cleaned at the close of the day, all waste picked up and placed in safety cans, all containers covered and every precaution taken against dirt and fire, the chief enemies of industry in general and of the lacquerer in particular.

Preparing the surface to be sprayed is of great importance. It has been touched on before, but can be mentioned again. Metal pieces such as steel panels, brass tubing, etc., should be free from all oil and grease, and this best accomplished by dipping in a tank of naphtha, or if the fire risk of this method be considered hazardous, in sodium hydroxide or trisodium phosphate solution followed by rinsing with water and drying. The latter treatment is liable to discolor brass and the former is preferred for this metal. If old paint or varnish is on the surface it should be removed completely. Various means are employed for this purpose: the paint may be burnt off by a blow-torch, softened by paint remover and scrubbed off or sprayed with a hot solution of soda or trisodium phosphate. Sand blasting has been used to good effect in removing paint, varnish and baked enamel from automobile bodies. In most of the refinishing stations the washing with hot caustic solution has been found most speedy and economical. It has an advantage over paint remover in price, and in that the thin film of wax that is left by the patented removers is absent with caustic solutions. A water wash thus suffices to clean off any residual caustic, while a gasoline wash would be required by a wax-containing remover. The metal should be thoroughly dried and the priming coat applied quickly to prevent rusting of the metal.

Wood surfaces should be thoroughly seasoned and sanded smooth before applying filler, lacquer or enamel. A second

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sanding is usually given after the first coat and this removes any fibers that were overlooked the first time as well as the excess of filler. If the sanding is done with paper moistened with water it is necessary to wait until the wood has dried thoroughly before applying the next coat.

Attempts are often made to apply lacquer on top of varnish coats either directly or after interposing a film of shellac. These attempts have met with some success but there is always the possibility of the lacquer solvents penetrating the varnish and lifting it up or peeling it. If possible the varnish should be removed and the finish built up from the beginning with lacquer materials, with or without the use of specially designed oil primer.

Some metals, such as die-casting metals, contain large amounts of oils firmly fixed in the microscopic pores. It is very difficult to enamel such materials unless the oil is first removed by sweating or heating to 200° to 300° F. for several hours. Even after this treatment many enamels will not adhere to the peculiar surface presented by these metals and special formulae must be developed. Glass is also difficult to enamel, even after thorough cleaning, and most enamels will crack off in a fairly short time.

Besides the usual one-color finishes, lacquer enamels can be used to produce other art effects. For instance, by enameling first with a light ivory and then rubbing with a little burnt umber in oil an excellent old ivory finish is obtained that is in wide use for ornamental iron work such as smoking stands, lamps, etc. On material of irregular surface two-toned effects can be obtained by first applying a lacquer enamel and then any desired second color in the form of an oil-benzene paint. By rubbing off the high lights while the second coat is still wet, pretty finishes are obtained. The so-called Mercury gold finish is obtained by spraying the brass or other ware with a yellow enamel in which "fine gold" bronze powder has been mixed. The high lights are rubbed down, a paste of paris green and ochre in linseed oil and turpentine is rubbed in, and

a clear lacquer sprayed to protect the finish. Italian gold is a finish obtained by first spraying a red enamel, then covering with "fine gold" bronze powder in a good bronzing liquid, and rubbing in with burnt umber in turpentine. The combination of the red back-ground, gold powder and umber glaze gives a very pretty effect.

Stippling, or the production of a finish consisting of many minute projections can be produced by brushing a heavy enamel of the desired shade over the surface and then producing the effect by a stiff-bristled stippling brush lightly dabbed on the enamel while still wet. A somewhat similar effect can be obtained by spraying the enamel with a low pressure and a wide nozzle on a back ground of the same color.

The bleeding of certain lakes, particularly the reds, is sometimes utilized. By dabbing a little red enamel on a doll's cheek, for instance, and then spraying with a flesh-colored enamel, the red bleeds through to give a realistic tint to the cheek.

Wood effects on metal are obtained by simple methods of graining quite similar to those used in the wood-finishing industry. A priming coat of enamel is first applied, after which the graining color, generally a mixture of silica and umber ground in water, is rubbed on and given the appearance of a grain either by combing in straight lines or by a circular stroke with a sponge for walnut and similar wood effect. A protective and hardening coat of clear lacquer is then sprayed on and after rubbing down with corundum paper a close imitation of wood grain is obtained.

A wide variety of other finishes has been produced by the use of lacquer and each veteran spray man knows a few which he jealously guards. They are more interesting than valuable, as the total amount of material used in trick finishes is insignificant. They are mentioned merely to show the wide applicability of the lacquer enamels.

One rather important and widespread custom is that of spraying a coat of thinner over an enameled surface. Prop-

erly done, this eliminates sags and wrinkles and gives a much smoother finish than otherwise obtained, while if carelessly applied it necessitates a re-finishing of the surface.

Lacquers are generally air dried, but occasionally a speed of production is demanded that necessitates forced drying. A temperature of 80° to 110° F. is sufficient for almost all lacquers and only a few minutes are required. High temperatures cause bubbling, pin-holing and peeling of the lacquer if applied before most of the solvents have evaporated.

### LACQUER FINISHING PRACTICE

#### Finishing of Wood.

One of the first things discovered in the finishing rooms of furniture factories when lacquer was introduced was that the wood required much more careful preparation than with varnish. Roughnesses and defects that were buried under the massive film showed up cruelly under the low-bodied wood lacquers. On the other hand it was discovered that well-sanded wood gave a beautiful rubbed or polished finish with a surprisingly thin film of good lacquer. Since the thicker the film of finish the more likely it is to crack, check, or shrink, not to mention the increased cost of material, it soon proved a great economy to spend time and labor on preparing the wood. This means careful and thorough sanding, sponging off of woods like mahogany and walnut that are especially subject to lifting of the grain when stained, careful filling with the proper filler and sealing of the filler by means of a thin coat of shellac or a mixture of shellac and lacquer. On this properly prepared surface lacquer shows its advantages best, and while much lacquer furniture is made without all this care, the tendency is more and more to thorough preparation of the wood. This has become more and more important as the veneers used became thinner and thinner; much of the furniture veneer to-day being as thin as  $\frac{1}{32}$  of an inch.

Careful gluing and drying is required if such a veneer is to be used successfully.

### Staining of Wood.

Some woods, such as birch and maple, are often left unstained and finished in pale lacquer so as to maintain the original appearance of the wood. Most furniture, however, requires staining of the wood to give an acceptable finish and with the exception of certain asphaltum stains to give shades of yellow and brown, and the natural dyestuffs such as logwood, fustic and archil, and chemical stains such as fumed oak, sodium bichromate on mahogany, picric acid and a few other isolated cases, the bulk of the stains used are the aniline dyes. Three types are used, spirit stains, those soluble in alcohols; oil stains, soluble in hydrocarbons like naphtha or benzol, and water stains.

The spirit stains are the most fugitive to light and with the exception of nigrosine are little used under lacquer. Oil stains, which generally have a stearic acid base, are very penetrating, give rich, bright tones, do not raise the grain, but with a very few exceptions are insufficiently fast to light for safe use. These are being improved continually, and it is the author's belief that they will eventually become the most widely used form of stain. The stearic acid is sometimes in excess, and this seems to rot the lacquer. An intermediate coat of shellac is a great help in such cases, as well as in those where the lacquer solvents bleed the stain.

At present most wood finished in lacquer is stained by water-soluble dyes. These are the most permanent to light and inert to lacquer but raise the grain even of well-sanded wood to a rough fuzz. The common practice here is to spray a thin coat of shellac on the stain, so as to stiffen the fuzz, and then sand smooth with sandpaper. Besides entailing two extra operations and the expense of the shellac, this procedure seldom gives as attractive a finish as an oil stain does.

It has been found the addition of such materials as glycerine or ethylene glycol diminishes the tendency of water stains to lift the grain, but they also introduce an uncertain factor as to the durability of lacquers over these slowly-drying solvents. Water stains are used in proportions from 2 to 10 ounces of the dry stain to a gallon of water warmed to about 80° F. After solution the stain is filtered through cheesecloth and used as soon as possible. The temperature of solution should be kept constant and weighings of the powders should be accurate to a small fraction of an ounce to keep uniformity of shade. Stain powders should be purchased from only the most reliable manufacturers and preferably from the manufacturers of the dyes, as they are open to much adulteration with soluble earths such as walnut crystals, which have practically no tinctorial strength.

Stains may be applied by dipping, spraying or brushing, but the last method is by far the one most frequently used. Dipping is used on chairs in many factories, and spraying of stains is sometimes done to give high-light or antique effects.

### Filling.

Stains are usually allowed to dry overnight before filling. Close-grained hard woods such as maple and birch are often left unfilled, but walnut and mahogany are almost invariably filled. The best type of filler is composed of hard quartz silex ground in a mixture of varnish-maker's linseed oil and kauri japan, thinned with a mixture of naphtha and turpentine. Many manufacturers wisely make their own filler, buying the japan from the varnish makers and their other materials on the open market. Not only is an economy effected but a much closer control of the all-important filler is obtained. Competition is so keen in the filler business that all sorts of adulterated and dangerous mixtures are offered to the unwary buyer at an apparent saving. The silex must be dry and free from such adulterants as clay and gypsum. The filler pastes are either made in a dough mixer or by grinding the silex

into the oil and japan in a stone mill. The latter is a more effective but much more expensive method. Filler should be kept on hand in tightly closed receptacles in heavy paste form and thinned accurately just before use. It is almost always brushed on the wood, allowed to set for five to ten minutes, and then dabbed into the pores with a pad of burlap, New Zealand hemp or similar fibre. It is next wiped off cleanly with clean cloths and allowed to dry overnight. Some manufacturers of pianos and other furniture double-fill their work, but single filling is adequate in almost all cases.

From the filler on there is a wide divergence in methods. The systems used vary from one coat of imitation shellac followed by a skimpy one of flat lacquer, to five or six coats of lacquer sprayed several days apart, then rubbed by hand to a perfect piano finish. The average finish can be summarized as follows: stain, fill, one coat 4-lb. bleached wax-free shellac, one or two coats of gloss wood lacquer, and either a coat of flat lacquer or a rubbing and polishing. So-called wood lacquers vary from a cheap Manila or Pontianak solution baptised by a trace of pyroxylin, to well-proportioned blends of pyroxylin, dammar or shellac resin and plasticiser. They generally come ready to spray and contain from 18-22 per cent total solids. Spraying pressures vary from 45-75 pounds, depending on the type of equipment used, type of lacquer and the taste of the finisher. An average pressure of 60 pounds seems to be a safe working basis.

The flat lacquers on the market vary immensely in quality. Some are very rubbery or cheesy, while the good ones are as hard and tough as the gloss lacquers and do not gray or haze the work. The best of them give a remarkable likeness to a rubbed finish at a tithe of the cost. They are invaluable on turned or carved parts where rubbing is expensive and tedious. The usual rubbing medium is a mixture of fine pumice and paraffin oil, although pumice and water are often used. Polishing is done with rottenstone and water or oil, although many proprietary polishes are available and used.

### Enamelled Furniture.

Much furniture is now produced in colors, and the lacquer finish is rapidly displacing the varnish enamels wherever the maximum gloss is not required. Several systems are in vogue, the chief one using a first coat of flat oil primer of about the desired shade and in a vehicle inert to lacquer, followed by one or more coats of lacquer enamel. A high gloss is obtained by spraying clear lacquer over the enamel, while the satin finish so popular now is obtained either in the enamel itself or by spraying flat lacquer over it.

Colored furniture is often embellished by high-lighting with a brownish-black lacquer, about the edges, by striping, and by decalcomania transfers. Much is now being finished in crackle lacquer of various color combinations. Reed or fibre furniture is often finished in lacquer enamels followed by a frosting or glazing with oil or japan colors which are sprayed on and wiped off the high-lights, giving a pleasing contrasted effect.

### Wood Turnings.

Broom and brush handles, toys, etc. of wood are often finished in lacquer by dipping. Either clear or colored lacquered lacquers may be used and the lacquer is generally of very high viscosity so that one or two coats will be sufficient. White often requires three or four coats, but then gives a finish almost identical with celluloid. Broom handles are almost invariably finished by dipping into a very heavy lacquer and withdrawing through a rubber gasket that wipes off the excess and leaves a smooth uniform coat. Pencils are often finished the same way, although some makers use the dip-and-drain method. Pencil manufacturers are very chary of divulging their finishing systems, so exact information must be gotten from subterranean sources.

Wooden objects to be dipped in lacquer are often prepared by tumbling in a rotating barrel with a highly pig-

mented silex oil filler. This closes the pores and effects a great economy in lacquer. Drippings are usually salvaged by collection on an amalgamated tin plate and redissolving in thinner. A slow regular speed of withdrawal gives the best results, but production demands in many industries require material that will permit of a rapid dip and withdrawal. Some objects are dipped and drained in the same position; others are dipped and then turned. Ingenious machines for handling turnings have been developed and remarkable outputs at low cost are possible.

### **Finishing of Metals.**

It may be said that there are two distinct types of lacquer finishes for metal. The first and oldest is the finishing of silver, brass and copper, either with clear or pigmented lacquers; and the other is the finishing of steel and aluminum automobile bodies, filing cabinets and similar articles.

The first method uses no primer, the lacquer adhering sufficiently well to permit of spraying directly on the metal, which has usually been thoroughly cleansed of grease, water, etc. A thin coat of clear lacquer is given most silver-plate, polished or brushed brass or copper articles to preserve the finish from tarnish or oxidation. By the introduction of bronze powders or pigments various decorative effects are obtained, elaborated in the lighting fixture industry by ornate shading, glazing stippling, spattering and polychroming, a full description of which is out of the scope of this book. This industrial use of lacquer is old and well established and the technique has been well standardized.

The finishing of large steel articles with lacquer is more recent and more important. Automobiles and filing cabinets receive rigorous treatment, often abuse, and the finish must stand up. The adhesion of the lacquer films to bare steel or aluminum is insufficient for this type of work and they are almost always given a priming coat of an oleoresinous nature, with such pigments as red oxide of iron incorporated both

as anti-rusting agents and to show the sprayer that he has completely covered the work. The primers should be baked, and in large production shops elaborate conveyor oven systems have been developed that permit of baking with incredible rapidity. Air-drying primers are available, although not quite as good as the former type; and these are widely used in refinishing shops and small factories. For steel office furniture a green primer, often on a chromium oxide base, is used under the prevalent olive-green shades.

During the manufacture of automobile bodies and similar objects, many tool marks are invariably left in the metal. For a smooth finish these are filled by the use of surfacers or fillers, on an oil or now more generally on a pyroxylin base. One to four coats of surfacer, a lacquer containing a high percentage of pigment, are sprayed on and sanded down to a smooth glass-like finish before the lacquer coats are applied. The number of lacquer coats varies widely, from 2 in some of the cheaper cars to as high as fourteen in the higher-priced machines. The cheaper cars are seldom rubbed or polished to any high degree, while the better ones are painstakingly sanded, rubbed with pumice stone and water, sprayed with thinner to heal the scratches, and hand polished to brilliant lustre with one of the several polishing pastes developed for the purpose. For spraying automobile lacquers pressure tanks are generally used with 4-8 pounds on the tank and 75-100 pounds pressure on the gun. Considerable work is being done on developing lacquers that do not give the so-called orange-peel effect, with much success. It is quite possible that the near future will see lacquers that will require neither rubbing nor polishing to give a satisfactory job. These may be sprayed, or they may be flowed on from a hose with a long narrow slit in the nozzle. The various manufacturers of automobile lacquers have issued numerous booklets on the technique of automobile finishing, available to all interested, and while sometimes with a natural bias to their particular product they are in general sound and informative.

The high gloss obtained with body finishing varnishes is as yet unobtainable with lacquer. Very durable clear lacquers for use as a top gloss coat has been very recently developed but it will take time to see if actual practice bears out the laboratory results. Even these materials lack the depth obtainable with varnish, and the very highest priced cars, whose buyers demand the old-time finish, are still varnished, sometimes over lacquer color coats.

### Grained Effects.

Wood finish effects on metal are frequently found on office furniture radiator shields and cabinets, battery boxes, etc. Almost invariably the finish is secured by using a ground coat of the proper shade for the walnut or mahogany effect desired, generally of an oleoresinous nature and baked on. This is followed by the graining color, usually colors ground in distemper or japan, and grained either by hand or by one of the photo-engraving processes now available. This is followed by two or three coats of gloss lacquer, which may be rubbed and polished or left as sprayed on the cheapest work. A coat of flat lacquer over the graining is used on metal beds, furniture, etc. and gives a rubbed wood finish very cheaply.

## CHAPTER XII

### MISCELLANEOUS ANALYTICAL METHODS

#### Specific Gravity.

The use of the pycnometer for determining the specific gravity of liquids and pigments has been described in Chapter VII. For thick viscous pastes this type is unsuitable and a modified simpler form is used. This consists of a wide-mouthed bottle holding 25 or 50 c.c. into which a ground glass stopper fits snugly. A hole is drilled through the center of the stopper. For determining the specific gravity of heavy pastes the bottle is weighed, filled with the material and the stopper forced into place. The excess material comes through the hole and is carefully wiped off with a rag moistened with solvent. The volume, previously determined by filling with water at a definite temperature, being known, the specific gravity is found by dividing the weight of paste by the volume.

#### Apparent Specific Gravity.

It is often desired to know the apparent specific gravity of a powder, that is, the weight in pounds of a gallon of the loose material. This varies, of course, with the fineness of the material and the volume of the air spaces and is a very difficult value to determine accurately. A close approximation can be made by using a standard brass box of exactly one cubic inch capacity. This is counterpoised, filled with the powder which is lightly tapped and smoothed flush with the top of the box. The weight thus obtained, multiplied by the proper factor, gives the apparent density in pounds per gallon. If the weight is taken in grams the factor is 0.5098.

### Analysis of Lacquer Solutions.

The complexity of modern lacquers, containing as they do from 3 to 10 different liquids as solvents and diluents, pyroxylin, resin or a mixture of resins, oil, plasticiser and possibly dyes or pigments, makes a quantitative analysis practically impossible. If the viscosity, percentage of pyroxylin, percentage of resin and plasticiser and amount of pigment be determined, and in addition the boiling range of the solvents be obtained, sufficient proximate data are usually obtained to permit of a close duplication of the material analyzed. Too much of this has been done by lacquer makers whose idea of research consists in securing samples of a saleable lacquer made by a competitor, analyzing it and duplicating it as closely as possible. Progress cannot be made in this manner, and it is far better for the manufacturer to carry on his research from the bottom up and thus be prepared to make up any desired material from the result of his researches. It is this ignoring of fundamentals that is causing much trouble among some of the old-line varnish houses who are dabbling in lacquer, and what they have saved in a research staff has been paid out many times in damages, complaints and loss of prestige.

Analysis of products by large consumers is increasing in frequency, and is a desirable practice to avoid cut-throat competition marked by the foisting of inferior products on the buyer. In Circular 227 of the Research Institute of the Paint and Varnish Manufacturers' Association, Gardner gives an excellent outline of the procedure employed by him, which is practically that of most companies in this field. An excellent article by Conley on the same subject has previously been mentioned, and Zimmer's article on "Analyse der Zapon und Zelluloidlacke" in *Kunststoffe* 3323 (1913) is of value, although considerably behind the times as far as modern lacquers go. Since almost any organic solvent or inorganic pigment is liable to be found, any analytical outline must be restricted to

those most commonly met with. Pigment analysis can be qualitatively and quantitatively analyzed by the methods of analysis of inorganic chemicals as given in such books as Treadwell-Hall or Scott. For resin analysis the reader is referred to Coffigner's book on Varnishes or Dietrich's "Analysis of Resins" (Scott Greenwood, London, 1920). Lewkowitsch's famous book on Oils, Fats and Waxes gives complete information on these ingredients and their analysis. For the detection and estimation of alcohols, esters and hydrocarbons Allen's Commercial Organic Analysis (Churchill, London, 1924 edition) is still the standard reference. The list could be extended but since more thorough examination can scarcely be carried on by other than a skilled chemist and since he undoubtedly is familiar with his references, there is small need of amplifying the bibliography.

Rough and ready tests are sometimes of great value. By flowing or spraying the material under examination upon a smooth glass or metal plate and noting the coverage, time of drying, nature of film—whether smooth, wrinkled, pinholed, etc.—and by testing of the dried film with the finger-nail a very good idea of the basic make-up of the lacquer can be obtained by a skilled chemist. The odor of the escaping solvents and of the dried film may offer valuable indications. Butyl, amyl or ethyl acetates can readily be recognized even in the presence of much hydrocarbon, and the presence of coal-tar or petroleum hydrocarbons can also be detected by the nostril. Acetone oil is very easily detected, even when attempts to mask it with safrol or wintergreen oil are made. Furfural is likewise unmistakable when once smelled, and camphor can scarcely be overlooked. The presence of disguising scents such as the above mentioned generally signifies an unpleasantly smelling ingredient and thus gives a clew even when successful in its primary purpose. Elemi gum gives a characteristic odor to the film, as does tung oil.

All material should be tested for acidity by evaporation on a bright copper or brass dish as previously described.

### Total Solids.

This value is very important, as it is a measure of the actual film-forming contents of the lacquer. It is generally obtained by evaporating a weighed sample in an aluminum box or on a tin can lid and weighing the residue. The material should be spread in a thin layer to avoid the formation of a thick skin which prevents the residual solvent from reaching the atmosphere. The skin should occasionally be pierced by a sharp needle to afford a vent for the vapors. Gardner gives a somewhat more accurate method whereby 100 c.c. of a 2 to 1 ether-alcohol mixture is added to a weighed 5- to 10-gram portion of the lacquer and the mixture stirred to homogeneity. The material is brought to a boil over a steam bath and 25 c.c. of water added with constant stirring, and the pyroxylin thus precipitated in a stringy form. The solution is evaporated on a steam bath, and then dried at 100° C. for two hours, cooled in a desiccator for  $\frac{1}{2}$  hour and weighed. Special precautions are necessary in lacquers containing camphor.

The film left upon evaporation gives some valuable data. A brown, brittle film indicates the presence of considerable resin, a soft oily one that of much oil or other plasticiser. Oil or resin can be removed from the film by exhaustion with chloroform or pure ether in a Soxhlet fat extraction apparatus, although there are some resins which are difficult to get in solution by these means. A chloroform exhaustion followed by one with absolute alcohol gives fairly good results unless the pyroxylin happens to be of the alcohol-soluble type. The combined extracts are evaporated down in a tared crystallization-dish and the increase in weight indicates the amount of the resins, oils and plasticisers present. If an original sample of 10 grams of lacquer was taken, and the total solids weighed 1.25 grams, we have a value of 12.5 per cent total solids by weight. If a gallon of the lacquer, as determined by finding the specific gravity and multiplying by 8.337, weighs 7.85 pounds, then the total solids weigh 0.981

pound to the gallon. If now, the weight of the combined resins and plasticisers is found to be 0.35 gram, that of the pyroxylin itself is 0.90 gram, and it can easily be calculated that the solution contains 0.705 pound of pyroxylin and 0.276 pound of resin and plasticiser to the gallon.

For a complete analysis of these combined resins and softeners the reader is referred to the books mentioned above. The analysis will be very tedious and almost certainly inaccurate except in a general and qualitative way. Certain materials can be determined with precision, such as the aryl phosphates, e.g., lindol. By saponification of the film with alcoholic potash potassium phosphate is obtained and this can be determined accurately by the phosphomolybdate method. The saponification and acid numbers, as well as the iodine number of the material can be determined and some opinion of the constituents secured thereby, although a mixture of dammar, ester gum, castor oil and butyl phthalate, for instance, presents analytical difficulties of a peculiarly difficult nature.

### Solvents.

One hundred to two hundred grams of lacquer are placed in a round bottomed pyrex flask and distilled with steam. This can be done by passing steam through the liquid or by adding 200 c.c. of distilled water and distilling from an oil or paraffin bath. If a thin solution is used and great care observed, the solvent can be distilled off directly, without the use of water, but in most cases steam distillation is required. The distillate generally forms two layers, a homogeneous one indicating that the solvent was of the absolute alcohol-absolute ethyl acetate type—as this mixes readily with water. The addition of salt to saturation will result in much of the ester and alcohol dissolved in the water layer being forced into the upper oily layer. This is separated off, dried over calcium chloride and fractionally distilled. Portions are taken at

10-degree intervals and the saponification value determined, as well as the percentage insoluble in 95 per cent sulfuric acid in the old. From the boiling point range, saponification value, and percentage of insoluble material (petroleum or coal tar hydrocarbons) the composition of the solvent can be roughly estimated. The water layer can likewise be fractionated, and alcohol (wood, denatured and sometimes butyl) can be found. Acetone also appears in the lower boiling fractions, either having been added as such or as methyl acetone. It can be detected qualitatively by warming a little of the liquid with sodium hydroxide and adding a drop of ortho-nitro-benzaldehyde, which forms a blue precipitate of indigo with acetone. Quantitatively it is determined by the Messenger method as outlined in Allen.

### Pigment Separation.

Mere dilution of an enamel, followed by filtration or even by ordinary centrifuging, does not often give a complete separation of a finely ground pigment from its lacquer base. The pigments, especially such fine ones as carbon black or red lakes, are very resistant to complete removal from lacquer solutions. By precipitating the pyroxylin with chloroform or water the combined pigment and pyroxylin may be brought down in slimy masses, from which, after redissolving the pyroxylin in acetone to a very thin consistency, the pigment can be separated by a few minutes' whirling in a centrifuge. It can thus be separated off and weighed, and the weight per gallon of original enamel found. Qualitative and quantitative determination of the ingredients can be made as outlined in the references mentioned above.

Another method for determining pyroxylin and separating it from the other solids in an unpigmented lacquer consists in diluting a weighed sample, 5 to 15 grams, with a mixture of equal volume of acetone and benzol until fluid. Twice the volume of chloroform is then added with constant stirring and

the precipitated pyroxylin filtered off on a Buchner funnel, using a tared 7 cm. filter paper. The paper and pyroxylin are washed with chloroform, dried at 100° C. for 2 hours and re-weighed. Increase in weight  $\times 100$  weight sample = per cent pyroxylin by weight. If much resin is present, some of this may cling to the pyroxylin and it will be necessary to redissolve the precipitate in a minimal quantity of acetone and benzol mixture, reprecipitate with chloroform and filter, dry and weigh as before.

The filtrates contain gums, resins and oils and can be evaporated down to small bulk over a steam bath, transferred to a tared crystallizing dish and evaporated to dryness. From this point the procedure is analogous to that first described.

From these data a close approximation to the analyzed lacquer can be built up, and a determination as to whether it adheres to specifications or not can be made. It is to be hoped that lacquers will soon be bought more widely on definite specifications, and it will undoubtedly happen when purchasing agents become more familiar with the materials and their value and tests.

Certain tests are often made even now. The viscosity is determined, either accurately, or by the judgment of the sprayer who accepts or condemns it as too thick or, more often, too thin. A frequent test for coverage is to dilute the enamel with  $\frac{1}{2}$ , 1, 2, and  $2\frac{1}{2}$  parts of thinner and spray over a standard piece of tin. The degree of dilution attainable with a satisfactory one-coat job is a measure of the coverage, at least as far as many spray men are concerned. A more accurate way is to use a large piece of steel, tin plate, or galvanized iron—say a square 4 ft. by 4 ft. A weighed amount of enamel is placed in a spray gun, thinned to proper consistency and sprayed so as to cover the metal to the sprayer's taste with minimum material. When the material is exhausted, the area covered is measured, and the number of square feet to the gallon coverage determined. Parenthetically it may be remarked that cheap lacquer enamels have from

the falling ball method will continue to be the lacquer room method among the smaller makers.

This viscosimeter is provided with a hard rubber cap to prevent evaporation of the liquid, and since it is not necessary to look through the liquid it can be used for enamels of any color or for lacquers containing air-bubbles, lint or what not. The details of set-up, adjustment, calibration and calculation are somewhat complex and the reader is referred to the pamphlet issued by the makers of the instrument.

### The Ford Cup.

This simple device is the standard means for testing the viscosity of varnishes and japans used by the Ford Motor Co. It is a cylindrical cup of polished steel, drawn to a conical shape at the bottom. A small hole is bored in the bottom. The cup fits into a circular gutter which serves to catch excess liquid. The cup is filled with liquid at 23° C., the hole being stopped by the finger. The time required for the liquid to flow out through the hole is a quickly obtained arbitrary value of great use in plant control.

### Color.

Many pyroxylin solutions, and some of the solvents and oils have yellowish colors and it is often desirable to have some absolute method of describing them. A simple method is to make up solutions of caramel in water of various concentrations, ranging from a very light yellow to almost a brown, add a little salicylic acid as preservative, place in glass tubes of uniform diameter, stopper and mount on a board. By placing an equal volume of the liquid to be tested in a tube of similar dimensions it is an easy and rapid task to find the standard that most closely approaches it and thus to record the color. A more accurate method is the use of the Lovibond tintometer or Duboscq or similar colorimeters, but this is seldom required.

### Acidity.

The acidity of a lacquer can be determined by shaking up 10–12 grams of the lacquer with ten times its volume of freshly boiled distilled water, filtering off the precipitated solids and titrating the filtrate with N/20 sodium hydroxide using phenolphthalein as indicator. The water should be freshly boiled and hot and the titration carried on rapidly to avoid error due to carbon dioxide from the air.

### Blushing.

The common method of comparing lacquers for resistance to blushing is to pour equal quantities on watch-glasses and allow to dry while occasionally breathing on them. This is, of course, very crude, and more accurate method is desirable. Good results can be obtained by rigging up a tight wooden box divided horizontally in two compartments. In the lower one a shallow pan of water is placed, over it a perforated metal or wooden partition and on the partition the material to be tested, which is flowed or sprayed on glass plates. A hair hygrometer and a thermometer or a wet and dry bulb thermometer in the box serve to record the temperature and humidity, while a small fan in the upper compartment keeps the air uniformly stirred. By means of an electric heater the temperature of the water and also of the apparatus as a whole can be raised to the desired point. Since blushing is generally only to be feared on warm, humid days lacquers should be tested at from 70–100° F. and 70–95 per cent humidity. Blushing of cheap lacquers under these conditions evidences itself as an opaque white coating, while those containing higher grade solvents may show only a faint rim of white under the most adverse conditions. A lacquer that will dry to a film of this type at 90° F. temperature and 90 per cent humidity can be sold as a high-grade non-blushing lacquer. In some cases, where small amounts of high boiling solvents are pres-

ent, an initial blush will appear that gradually clears up as the excess of non-solvent disappears and the high-boiling component begins to assert itself.

A modification of this apparatus consists of a tight box through which air is drawn after passing through a series of washing bottles. Air passing through a water bottle will be saturated with moisture, while that passing through concentrated sulfuric acid will have practically zero humidity. A concentrated solution of salt gives about 80 per cent humidity, while mixtures of sulfuric acid and water can be made to give the exact humidity desired between zero and 100 per cent. It must be remembered that warm air can contain more moisture than cold, and that provision should be made for heating the box and the washing bottles to the required temperatures. Another point to remember is that the pressure of the air in spraying affects the blushing propensities of a lacquer, a high pressure causing a much more rapid volatilization with consequent chilling of the liquid and condensation of moisture.

### Appearance of Film.

Spraying and flowing on glass that has previously been carefully freed from grease and dirt and wiped clean with a lintless towel are the best means for judging the flowing qualities and freedom from specks of a lacquer. A good product should give a perfectly clear, colorless film, free from wrinkles or puckering. The presence of dirt specks can be more easily determined by the use of a microscope or by placing the glass in a projector which throws a many times magnified image upon a screen.

### Odor.

The odor of some solvents is persistent, which is an undesirable trait except in such cases where the odor is required to kill more offensive smells, such as in leather dopes,

or where it is required as in the cedar oil lacquers used to impart the smell and appearance of cedar to other woods.

No odor should be perceptible within 8 hours after spraying, while many users refuse a lacquer which retains an odor even an hour after application. The limits vary with the user's other requirements.

### **Hardness.**

The hardness of a lacquer film is determined most generally by one of the most inaccurate of instruments, the lacquer sprayer's finger nail. By some process of evolution the hardness and penetrating power of these finger-nails has kept pace with the increased qualities of the lacquer, but they are obviously not instruments of precision. No real scientific apparatus, as far as the author knows, has been developed to replace the finger-nail, but a recent and interesting suggestion involves the use of a series of lead pencils of varying hardness. These are drawn over the surface of the film with approximately equal pressure and the one that penetrates the lacquer first characterizes its hardness. These work fairly well for varnish and paint films and the softer lacquer combinations, but the author doubts greatly if any lead pencil made can penetrate a really hard pyroxylin film.

It may be possible that some modification of the sclerometer can be devised which will give a real measure of hardness and such an instrument would be of much value in settling disputes between buyer and seller.

### **Testing Lacquers and Enamels.**

In Circular 226 of the Research Bureau of the Paint Manufacturers Association, Dr. H. A. Gardner describes an accelerated testing cabinet for use in testing paints and varnishes that seems quite applicable to the testing of pyroxylin products. The advantage of such a cabinet in securing infor-

mation as to the durability of a product in less than a quarter of the time required by ordinary exposure is obvious and some such device should be a part of every research laboratory's equipment. It consists of a revolving wheel upon which rectangular panels of wood or metal are fixed after having been sprayed with the material to be tested. The spraying should be as uniform as possible and should be checked up by a determination of the increase in weight of the panel.

The wheel is arranged to revolve at 2 R.P.M. The lower half of the wheel passes through a box cooled by refrigerating pipes to a temperature of below 20° F. The upper portion of the wheel passes through a spray of water simulating rain and then through a beam of ultra violet light produced by a powerful mercury-quartz tube. A battery of 100 watt bulbs, 12 in number give a heating and lighting effect comparable to a summer sun. The panels are thus given an intense treatment combining the action of rain, light, heat and cold, and at least a comparative estimate of the durability of finishes can be obtained in a short time. Some of the break-down of paint films has been ascribed to ozone, and this is generated to some extent by the ultra-violet light. Hydrogen peroxide, ammonia and sulfur oxide fumes are other naturally occurring foes to film-durability and it seems feasible to secure definite concentrations of these substances in the cabinet or in the water spray.

The effect of this treatment on enameled panels is apparent enough but the break-down of a clear lacquer film is not so easily observed. If the lacquer be sprayed on a smooth, clean piece of black iron, break-down of the film will generally show itself by rusting of the iron at the points of weakness. A precaution to be observed in testing wood panels is to be sure that sides and edges are lacquered or enameled, as otherwise there is danger of moisture seeping through the grain and lifting up the lacquer coat from below.

NOTE.—This pamphlet was presented at the annual meeting 1925, of the NATIONAL FIRE PROTECTION ASSOCIATION, and approved for printing as an advisory brochure. Minor changes in the report originally presented have been incorporated by the committee in accordance with the authorization by the annual meeting.

## PYROXYLIN FINISHES

### THEIR USE, AND SUGGESTIONS FOR SAFEGUARDING THE ATTENDANT HAZARD

Attention is called to the fact that there are separately published standard regulations governing the protection and installation of spray booths and other finishing processes. This report is intended to supplement these regulations and not to be a substitute for them.

1. The increased use of various enamels, lacquers or finishes having a nitrocellulose content, properly termed "Pyroxylin Finishes," has created fire hazards, which this report discusses. In the automobile and furniture industries the extensive use of these finishes is new, and it is probable that this development will spread to other industries.
2. As a rule the solvents used with pyroxylin finishes are in the alcohol class with low flashpoint. The total content of the solids included resins, pigments, flexible oils and nitro-cotton, the percentage of the latter being relatively small.
3. The hazard is similar to that introduced by the use of paints and varnishes. The most common method of application consists of spraying, and the hazards attendant upon flow coat work, dipping, enameling and baking are therefore absent. As the thinners employed are highly volatile, quick drying is a characteristic of these finishes, hence the hazard in general can be mainly safeguarded by adequate ventilation. Oxidizing oils are not as a rule employed, but where such oils are involved, the hazard of spontaneous ignition, as in the case of paints and varnishes, is present and should be guarded against.
4. The dried residue which collects in spray booths and ducts is highly flammable, and once ignited the resulting fire

spreads rapidly. The degree of this hazard largely depends upon the design and manner of installation of the ventilating system, operating methods and quality of housekeeping.

5. Necessary safeguards covering the features of installation and protection are included by the following recommended requirements of the National Fire Protection Association: Regulations governing Spray Booths, Regulations for the Installation of Blower and Exhaust System, Regulations governing the Protection of Openings in Walls and Partitions, the National Electrical Code, and Regulations for the Installation, Maintenance and Use of First-Aid Fire Appliances.

6. The Inspection Department having jurisdiction should be consulted before any definite action is taken in connection with the following: the introduction of pyroxylin finishes, relocation of existing equipment or departments, changing of existing equipment, purchase of new equipment, or the storage of pyroxylin finishes and thinners. If timely advice and guidance are secured in connection with the foregoing, unnecessary hazards will be eliminated, and in many instances, the necessity of making subsequent expensive changes obviated.

7. For convenience the necessary safeguards are described under two headings: Part 1, where these finishes are used in large quantities, for example, in the automobile and furniture industries, and Part 2, where used in limited quantities, such as in automobile refinishing shops, etc.

## PART 1

### USE OF PYROXYLIN FINISHES IN LARGE MANUFACTURING PLANTS

#### Main Supplies.

8. Main supplies of pyroxylin finishes and thinner should be stored in an outside storage house preferably of non-combustible construction or in a properly cut-off and protected

inside storage room. Thinner should preferably be stored in underground storage tanks, in which case the discharge pump should be installed in the mixing room, thereby facilitating handling the solvents and reducing the hazard by decreasing quantity of thinner present in the building.

9. An inside storage room should be avoided; where one is necessary it should be located at or above grade, and where practicable in a corner of the building. Special care should be taken to locate it away from sections having combustible and valuable contents. If situated over damageable materials or products, floors should be waterproofed, and provisions made for drainage to a safe place. If adjacent thereto, it should be cut off from the remainder of the building by walls or partitions. Such walls or partitions should be continuous from floor to ceiling, securely anchored and of one of the following types of construction:

Reinforced concrete.

Brick.

Expanded metal lath encased in solid cement plaster not less than  $2\frac{1}{2}$  inches thick.

Gypsum or cement plaster at least  $\frac{3}{4}$  inch thick on metal lath on each side of a stud partition.

Tile (gypsum, or concrete block (cement plaster on each side with thickness of  $\frac{1}{4}$  inch).

In lieu of the foregoing any type of partition construction may be used which will afford one hour's protection as determined by the specifications for standard fire tests of non-bearing partitions.

10. Ceilings, unless of fire-resistive construction, should be protected with  $\frac{3}{4}$ -inch cement or gypsum plaster on metal lath or its equivalent. Shelving and supports should be of metal or other non-combustible material.

11. All wall or partition openings should be protected by approved fire doors of a type suitable for use in openings in corridor and room partitions, and installed in accordance

with the requirements of Class C of the National Fire Protection Association's Regulations governing the Protection of Openings in Walls and Partitions against Fire.

12. Good natural ventilation is essential in all storage houses and rooms. Ducts should be of substantial metal construction extending above roof of building and terminating in an efficient suction-creating device and having screened openings at floor level.

13. Artificial lighting should be restricted to electricity, employing vapor-proof globes and with installation in accordance with the requirements of the National Electrical Code for extra-hazardous locations.

For heating purposes only indirect systems such as steam, hot water or hot air should be employed.

14. Room should be equipped throughout with automatic sprinklers.

#### **Local Supplies and Mixing Rooms.**

15. All mixing and thinning in quantity, except a small amount which may be necessary at spray booths, should be conducted in a room separated from the remainder of the building. (It should be borne in mind, however, that these suggestions do not contemplate the manufacture of pyroxylin finishes on the premises.)

16. Respecting such features as location of mixing room, wall and partition construction, protection of openings therein, ceiling construction, floor drainage, ventilation, lighting, heating and automatic sprinkler protection, the requirements set forth for inside storage rooms under "Main Supplies" should be complied with.

17. The mixing room should not be used for storage purposes. The quantities of pyroxylin finishes and thinner permitted therein should be dictated by the demands of normal spraying operations. Pyroxylin finishes should be kept in the mixing room until needed, and every effort made to reduce to a minimum the quantity present at spray booths.

18. All mixers, filters, pumps, motors, shafting, etc., should be electrically grounded in an effective manner.

### Spray Booths.

19. The location of spraying operations in relation to other departments is of paramount importance, as it is essential that this hazard be kept away from large values damageable by fire and water. Such operations should be located as follows, the locations being stated in the order of preference:

- (a) In separate buildings.
- (b) On ground floors of main buildings.
- (c) On upper floors. In this case where spraying operations are located above contents damageable by water or fire, the floor areas of upper stories occupied by such spraying operations should be thoroughly waterproofed, inclosed with raised ramps, or depressed drains and scuppers provided through all external walls to carry off water discharged in time of fire.

The National Fire Protection Association's rules governing spray booths should be observed in connection with the application of pyroxylin finishes. The following features are of pronounced importance and are therefore emphasized.

20. Spray booths should not be placed in rooms containing flames or spark-producing machinery unless separated by fire resistive partitions as described in "Main Supplies." Every effort should be made to locate spray booths away from combustible or damageable materials or products. Such booths must be of metal or of other non-combustible construction.

21. Ventilation must be sufficient to immediately remove flammable vapors. Installation should conform to the regulations of the National Fire Protection Association for Class B systems governing removal of flammable vapors as included in the regulations for the Installation of Blower and Exhaust Systems. Ventilating fans should not be stopped until all vapors have been eliminated.

22. Four general methods of ventilation in connection with Pyroxylin finishing processes have been met with in practice as follows:

- (a) Induced or syphon type, i.e., fans and motor entirely outside of booth and ducts.
- (b) Fans in duct but motor and bearing outside and shaft driven.
- (c) Belt-driven fan in duct and bearing and pulley inside, belt entering through opening in side of duct.
- (d) Fan, motor and their supports in ventilating duct.

These are listed in order of preference, the last method (d) being considered a dangerous arrangement which should not be used, and the third (c) an undesirable arrangement which may involve hazard and should be changed whenever possible.

23. Substantial construction should be the rule for stacks and vents: joints should be riveted and soldered or otherwise made tight. They should extend as directly as possible to the outside air and not through other rooms. Each booth should have an independent stack or vent.

24. Inspection openings and clean-out holes of sufficient size should be provided at upturn elbows and other places where accumulations may be expected. These may be used for fighting fire which might spread to interior of duct and should be at accessible points.

25. Under no circumstances should a dust-collecting system be used for ventilating purposes or vice versa.

26. Booths and where possible ducts should be provided with automatic sprinklers. Silica bulb sprinklers should preferably be used.

27. If there is a tendency for spray to collect on sprinkler heads they should be covered with small paper bags or tissue or thin waxed paper which should be changed at least once a week.

28. Where not practicable to install automatic sprinklers in ducts or stacks, or where there is danger of freezing, manu-

ally or automatically operated open heads should be provided. If manually operated, control should be located at accessible points.

29. In sprinklered buildings curtain boards should be provided between sprinklers in the vicinity of spray booths, so that in case of fire within the latter sprinklers elsewhere will not be affected.

### Spraying.

30. Three methods of spraying are in use, viz., continuous circulation system, pressure tanks, and gravity feed from container to air gun or from receptacle attached directly to air gun. Where continuous circulating systems are used, mixing tanks, filters and pumps should be located in the mixing room. If located within this room, motors should be of vapor-proof type with provisions for remote control at a readily accessible location.

31. Receptacles containing pyroxylin finishes or thinner for pressure-tank systems should be returned to the local mixing room at the close of each day. Such pails should not exceed 10-quarts-capacity for gravity feed to air brushes and should be kept covered with tight fitting non-combustible covers. Wire cables or those containing stranded wire cores should be used to support gravity-feed receptacles. No open containers should be permitted.

32. When necessary to use thinner outside of the main storage or mixing rooms, it should be restricted to small amounts and kept in approved type metal safety cans.

33. Experience indicates that it is practically impossible to adequately ventilate tunnels or keep them clean, hence the practice of using tunnels should not be permitted.

### Lighting.

34. Artificial lighting in spray booths should be restricted to the use of electricity with installation in accordance with

the requirements of the National Electrical Code for extra-hazardous locations.

### Housekeeping.

35. The necessity for good housekeeping cannot be over-emphasized. To this end spray booths, ducts and stacks should be kept as free from deposits as practicable.

36. For cleaning purposes only non-sparking implements are permissible. During the cleaning operations surfaces should be thoroughly wet down. Where used, metal spuds or hoes should be made of non-ferrous metal.

37. Three methods are in use for cleaning interior of spray booths as follows:

(a) A heavy coating of plaster of Paris or whiting.

(b) Walls and roof covered with a heavy coating of vaseline or cup grease over which is usually applied heavy manila paper.

(c) Interior blown down daily with compressed air while ventilating system is operating.

38. Cleaning operations should occur at least weekly. Scrapings should be placed in covered metal receptacles and immediately disposed of. As combustible dust can be ignited by friction or sparks, it is important that the floor of the booth including turntable, turntable track and rollers should be kept clean, even though it necessitates sweeping and removal several times during the day.

39. Employees must not be allowed to enter stacks or ducts for cleaning until the stacks or ducts are entirely free from flammable vapors and are thoroughly wet down for their entire length.

40. No smoking should be permitted at or near any spraying booth; this also applies to storage buildings, storage rooms in buildings and mixing rooms.

41. Spray booths used in connection with the application of pyroxylin finishes should be used for no other purpose. If

this caution is not observed, serious results will likely occur for the reason that alternating deposits of pyroxylin materials, varnish, oil base stains, ground coats, etc., make probable spontaneous heating and eventual ignition.

### **Fire Extinguishers.**

42. In addition to 2½-gallon soda and acid extinguishers, small hand hose, etc., foam-type extinguishers have proven highly effective in the extinguishment of fires in lacquers and pyroxylin finishes, hence it is advisable that one or more be immediately available at each mixing room and spray booth; where several large booths are grouped together a 40-gallon chemical engine of the foam type should be provided; this also forms a valuable means for protecting the mixing and storage rooms.

43. Sawdust and soda mixtures have also been found effective for controlling and extinguishing lacquer, oil and paint fires and where provided are a valuable adjunct to foam equipment. The following is quoted from the National Fire Protection Association's pamphlet on First Aid Fire Appliances:

Receptacles of special type (a substantial bin about  $1\frac{1}{2} \times 1\frac{1}{2} \times 3\frac{1}{2}$  feet high with reinforced edges and with sides tapered downward) made of galvanized iron or steel; of 8 bushels capacity; each provided with two or more scoop shovels with handles of suitable length. The extinguishing agent must be clean dry sawdust, free from dirt, chips, shavings and other foreign matter, thoroughly and evenly mixed with bi-carbonate of soda in the proportion of 10 pounds of soda to one bushel of sawdust.

## **PART 2**

### **REFINISHING SHOPS**

#### **Pyroxylin.**

44. If more than one day's supply of pyroxylin finish and thinner is kept in stock, it should be stored in a cabinet, tightly

enclosed and made of sheet iron at least No. 18 U.S. gauge in thickness and double walled with 1½-inch air space, or equivalent construction. Doors should be of construction equivalent to walls, provided with 3 point locks and kept closed when not in use; door sill should be raised at least 2 inches above bottom of cabinet. Cabinet should be vented 3 inches above the bottom and close to the top by a vent pipe having an area of not less than 10 square inches and made of metal not thinner than No. 22 U.S. gauge with lapped seams and riveted joints; vent pipe should be kept at least 6 inches from combustible material, extend directly to outside air and terminate in a hood or shield.

45. Quantities of pyroxylin finish and thinner exceeding 50 gallons should be stored outside; or if inside, in a small storage and mixing room separated from the remainder of the shop by walls of material and construction as indicated below, but under no circumstances should storage inside a building exceed 250 gallons.

46. Walls may be of the following construction and should be continuous from floor to ceiling and be securely anchored.

Reinforced Concrete.

Brick.

Expanded metal lath encased in solid cement plaster not less than 2½ inches thick.

Gypsum or cement plaster at least ¾ inch thick on metal lath on each side of a stud partition

Tile, gypsum or concrete block (cement plaster on each side to a thickness of ¼ inch).

In lieu of the foregoing any type of partition construction may be used which will afford one hour's protection.

47. Ceilings, unless of fire-resistive construction, should be protected with cement or gypsum plaster on metal lath or its equivalent.

48. Walls in frame buildings should be protected with cement or gypsum plaster on metal lath or its equivalent, as specified for ceiling.

49. Floors unless equal to 2-ply matched boards and free from cracks and other openings should be protected with 2 inches of concrete.

50. All openings should be protected with fire doors of approved automatic or self-closing type, suitable for use on openings in corridor or room partitions and conforming as to installation with the Class C requirements of the National Fire Protection Association's regulations for the Protection of Openings in Walls and Partitions Against Fire.

51. Artificial lighting should be restricted to electricity with installation in accordance with the requirements of the National Electrical Code for extra hazardous locations.

52. As previously indicated adequate ventilation is of pronounced importance and care should be exercised to ensure the installation of a system capable of completely removing the vapors and thereby preventing the accumulation of combustible mixtures.

53. Natural ventilation, such as ordinarily provided for oil and paint houses, is preferable. Ducts should be of substantial metal construction extending above roof of building and terminating in an efficient suction-creating device and having screened openings at floor level.

54. Thinner when obtained in metal drums should preferably be stored outside of building or in the above described storage and mixing room. Mixing operations should preferably be carried on in the storage and mixing room, but mixing operations on a small scale can safely be effected in the spraying room or booth provided the amounts exposed are reduced to a minimum and the ventilating system is in operation.

### **Spraying.**

55. Spraying should never be permitted in basement or below grade floor of a building. If individual non-combustible spray booths are not used, spaces in which cars or other materials are refinished should be separated from the remainder of the shop by partitions of fire-retardant construction such as wall

board on wooden studding, cement or gypsum plaster on metal lath on wooden studding or wooden studding covered both sides with galvanized iron or its equivalent. Doors at openings in spray-room partitions should be equal in fire resistance to the partitions and be of self-closing type or be installed so as to close automatically.

56. The ventilating system should be capable of effecting a complete change of air every three minutes and be provided for each spray booth or spraying room. Fans and exhaust outlets should be located several feet above the floor and discharge directly outside of building. Installation should be in accordance with the requirements of the National Fire Protection Association for Blower and Exhaust Systems for removal of flammable vapors.

57. If shop is so located that direct outside discharge cannot be obtained, ducts should be run directly outside of building and to a safe point above roof. If fan is direct motor driven, the motor should be of the non-sparking induction type and shielded to prevent vapors or dust coming into direct contact with it. If fan is belt driven, the motor should preferably be located outside of room or at least at ceiling of room. Motors should never be placed directly beneath floor of spraying room. In general, installation of all electrical equipment should be in accordance with the requirements of the National Electrical Code for extra hazardous locations. This will also require switches; fuses and rheostats controlling ventilating fans, all switches and fuses in connection with the lighting system or equipment and including air compressors to be located outside of spray booth or room. Belts and fan should be electrically grounded in an effective manner in order to guard against static electricity. All wiring should be in metal conduit and lights protected by vapor-proof globes.

58. The use of open flames or spark producing devices in storage and mixing rooms, storage cabinets, spray booths or rooms, or in close proximity to same should be prohibited. For heating purposes only indirect systems such as steam, hot

water or hot air should be employed. It is also important that spray booths or rooms be kept free from all unnecessary combustible material.

### **Housekeeping.**

59. Floors of spray booths or rooms should be thoroughly cleaned at least once a day and fans, ducts, side walls and ceilings kept as clean as practicable at all times. Fibre brooms or brass or bronze implements should be used for this purpose in order to avoid the creation of sparks. Where practicable surfaces cleaned should be sprayed or otherwise wet down with water before cleaning. Approved waste cans should be provided for all rags and waste which have come in contact with primer and surfacing coats or have been used in conjunction with paints or varnishes. Sweepings and deposits from spray booths or rooms, ducts or stacks should be disposed of immediately.

### **Fire Extinguishers.**

60. An adequate supply of 2½-gallon foam-type extinguishers should be installed at or near spray booths, storage cabinets and in or near spray rooms and storage and mixing rooms. Sawdust and soda mixtures as described in Part 1 are very effective for extinguishing fires in oils, paints, varnishes and lacquers and will be valuable in addition to foam equipment.

### **General.**

61. Cars being worked upon should not be moved by their own power after they leave storage section of refinishing plant. Smoking must be prohibited.

62. If the safeguards herein recommended are provided and ordinary care exercised in connection with operations, the hazard attendant to the use of pyroxylin finishes will be reduced to a reasonable and acceptable degree.



Regulations of the National Board of Fire Underwriters, as recommended and published in pamphlet form by the National Fire Protection Association, Edition of 1926.

## APPENDIX

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### REGULATIONS FOR PAINT SPRAYING AND SPRAY BOOTHS

#### DEFINITIONS

In these regulations the following words are used as defined below:

"Shall" is intended to indicate requirements.

"Should" is intended to indicate recommendations, or that which is advised but not required.

"Approved" refers to approval by the authority having jurisdiction in the enforcement of the regulations.

1. These regulations refer to the application of paint, varnishes, lacquers and like finishes by spraying with an air brush or direct pressure, which presents a severe fire hazard. Complete ventilation is required to dispose of waste residues and vapors from the process, to avoid an atmosphere which, if not explosive, permits the rapid spread of fire, with the probability that practically all sprinklers in the room where spraying is conducted will open. Spraying processes also require specially designed equipment to minimize the collection of residues, which are particularly hazardous where pyroxylin lacquers are used.

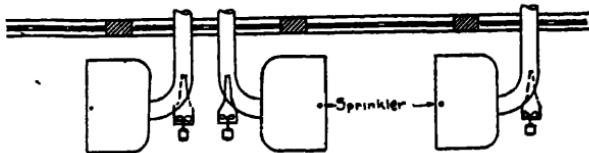
NOTE: Fires in spray booths result from four principal causes: First, fans and motors used for venting the booth; second, broken electric lamps and other electrical defects; third, cleaning interior of booths, fans and motors with highly flammable solvents; fourth, accumulation of deposits in the tubes and vent pipes, resulting from neglect to clean them frequently and from poor design.

2. Fires in this process are such as to demand a considerable amount of water to extinguish them and so the location of the process should not be over valuable contents subject to water damage unless the floor of the spraying room is waterproofed and provided with adequate scuppers or drains.

3. The process preferably should be located in detached buildings or one story additions and its location under smooth ceilings is advised as it is difficult to thoroughly protect open joist construction subject to such severe fire. It may often be advisable to sheath such joist construction over spraying rooms with cement plaster on metal lath or equivalent approved construction.

4. Spray rooms should be separated from other values as far as possible by non-combustible partitions, but care should be taken not to make the spray room so small as to increase the liability to explosive mixtures of vapors and air. Booths preferably should be located sidewise to the walls so that natural light may be obtained and that fires may be more readily extinguished by projecting hose streams through windows. This is especially important in unsprinklered properties.

**NOTE:** Curtain or draft boards, installed at the ceiling help to confine spray booth fires to a limited area and prevent the needless spread of heat, thereby avoiding water damage especially in sprinklered properties. Curtains should enclose an area considerably larger than that of the booths.



An arrangement of spray booths to minimize the necessity for artificial light and to permit full protection by hose streams through windows.

### **Booths.**

11. Spray booths shall be constructed of metal with heavy metal frame. The use of wired glass panels in part is satisfactory. The booth should be as smooth as possible inside to promote cleanliness. If combustible the floor within the booth and for an adequate distance outside should be protected with zinc or other metal (preferably not steel, that sparks may be avoided). There should be a curtain not less than  $2\frac{1}{2}$  inches and not more than 5 inches deep along the outer and upper edge of all booths.

12. Booths, if of steel, should be kept thoroughly painted or otherwise coated, especially the corners, to minimize the possibility of sparks.

13. Booths shall be separated.

NOTE: A combination of two or more booths permits fire to communicate from one to the other, involving more than one booth in a fire; such an arrangement is not standard.

14. Where necessary, baffle plates shall be of removable type to facilitate cleaning. They are not advised in connection with pyroxylin lacquer. Baffle plates should be taken to a safe place for cleaning.

### **Exhaust Systems.**

21. Exhaust systems should be in accordance with the regulations governing Blower Systems, in addition to the specifications herein.

22. Exhaust systems preferably should be indirect, the fans and source of power being located outside the booth and the exhaust pipe. If fans are inside, power shall be supplied by outside approved motors, air or water turbines, belts, or chain drives. If belts are used they shall be provided with a comb properly grounded to collect static electricity. Electric motors shall not be placed inside booths or exhaust pipes. Power for fans shall be arranged so as not to be interrupted by a fire in the spray booth, that the fans may be kept in operation during a fire to exhaust smoke and heat.

23. Exhaust systems shall be so designed as to maintain sufficient velocity and air circulation to adequately remove the vapors and to prevent all possibility of explosive mixtures forming in the room or the booth. Sufficient fresh air should enter the room to permit the fans to act efficiently and direct air currents toward the booths.

24. Each booth shall have an independent exhaust pipe.

25. Pipes and stacks shall be provided with doors with strong fastenings, or otherwise be accessible for cleaning. They should be kept from contact with combustibles, being treated as chimney flues.

26. Pipes shall terminate in a location where the discharge will not endanger property.

Where the building is so exposed that fire or sparks might enter the exhaust pipes setting fire to the spray equipment, the outlets shall be protected.

27. Where necessary spray rooms should have ventilation in addition to the fans for the spray booths, this ventilation preferably should be by natural means through wall openings at the floor level, windows and roof vents. If fans are used for ventilating the room,

the system shall be in accordance with the regulations for Blower Systems.

28. Fans shall have rigid brass, bronze, or aluminum blades with ample clearance to avoid creating fire by sparks or friction, necessary allowance being made for ordinary expansion and loading to prevent contact between moving parts and the tube; or if blades are of steel they shall be surrounded by a brass or other non-spark producing ring.

29. Fan motors shall be of a type approved for hazardous locations. Fans shall be mounted on a shaft sufficiently heavy to maintain perfect alignment even when the blades of the fan are carrying heavy loads of paint, the shaft preferably to have bearings outside the tube and booth. All bearings should be of the self-oiling type. Fans preferably should be kept running during a fire. (See Article 32, National Electrical Code.)

#### **Electric Equipment.**

41. All electric apparatus shall be in strict accordance with the National Electrical Code governing such apparatus in hazardous places. Only incandescent or mercury-vapor lamps shall be used for lighting. Lamps shall be protected by vapor-proof globes or shall be double glazed; no spark-producing cutouts, switches, detachable plugs, or portable lamps shall be used.

#### **General Rules.**

51. Solvents, paints, lacquers and such flammables shall be stored and handled in strict accordance with the Regulations for Containers for Hazardous Liquids so far as they apply and the main supply shall be kept outside the building.

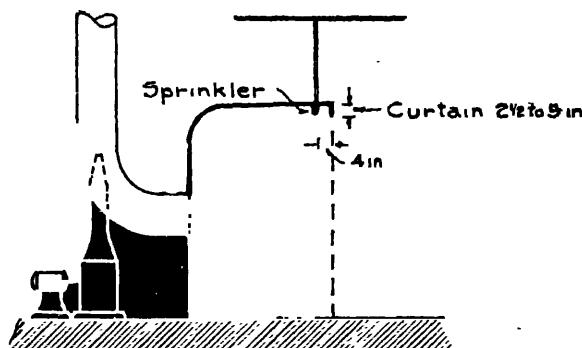
52. Containers supplying spray nozzles shall be of closed type or provided with tight-fitting metal covers kept in place. Tanks not resting on the floor shall be supported on metal brackets or suspended by wire cables. Gravity tanks shall not exceed 10 gallons. If an original container is used directly at the booth, it should be mounted on strong brackets which will hold it securely in place, while in use. Air pressure, if used on original containers, shall not exceed 10 pounds, a relief valve being provided on the tank attachment for this purpose. Empty drums and other empty containers shall be promptly removed from spray room.

53. Piping shall be strongly erected and rigidly supported. Valves shall be provided in pipes where flexible hose is taken off and these shall be kept closed when hose is not in use.

54. If a spray liquid heater is used, it preferably should be steam. If electric, it should be of approved design and arranged to prevent the attainment of a dangerous temperature.

### Protection.

61. Each booth shall be equipped with one or more approved automatic sprinklers, which may be supplied from the regular



Protection for spray booths. Shows automatic sprinkler and small curtain to confine water and heat to the booth.

sprinkler system, when available, or, in unsprinklered rooms, from the nearest convenient adequate water-supply pipe. Sprinklers should be located within the booth at the top, not nearer than 4 inches from the outer edge, so that they will not get covered with paint and can protect some of the area outside of the booth, but not nearer than 4 inches from the edge and close to the top of the booth. Sprinkler should be kept clean. A curtain not less than  $2\frac{1}{2}$  inches nor more than 5 inches deep shall be installed along the upper outer edge of the booth to serve as a deflector to confine most of the discharge in the booth and retain heat.

Vent tubes and stacks, unless very short or small, shall be equipped with one or more approved automatic sprinklers so located that the entire interior of the tube will be protected.

Booths of unusual design, shape, size or hazard require specially planned sprinkler protection; Inspection Departments having jurisdiction shall be consulted as to the required protection in such cases.

Automatic sprinklers within booths, vent tubes, and stacks shall be controlled by one or more approved valves located in a readily accessible place not seriously exposed to a fire in the booth.

62. FIRST AID. A standard equipment of first-aid apparatus shall be provided. (See Regulations for First Aid Fire Appliances.)

NOTE: Foam type extinguishers are particularly effective to protect open containers of flammable liquids. For the general protection of spray booths and their exhaust systems, particularly where pyroxylin lacquers are used, a standard equipment of small hose or of soda-acid extinguishers should be installed. Where the spraying hazard is extensive or severe, a 40-gal. chemical engine should be provided.

### Maintenance.

71. Spray booths, tubes, stacks and all other apparatus shall be kept as free from deposits as practicable by cleaning daily and oftener if necessary. For cleaning purposes, only non-sparkling implements are permissible. Where used, metal spuds or hoes should be made of non-ferrous metal.

Where pyroxylin lacquers are used, all surfaces of booths and tubes where dust accumulates shall be thoroughly wet before starting cleaning operations.

NOTE: The dried residue which collects in spray booths and tubes, where pyroxylin lacquers are used, is highly flammable, and once ignited the resulting fire spreads rapidly. The degree of this hazard largely depends upon the design and manner of installation of the system, operating methods, and quality of housekeeping.

Employees must not be allowed to enter stacks or tubes for cleaning until the stacks or tubes are entirely free from flammable vapors and are thoroughly wet down for their entire length.

Cleaning interiors of spray booths may be aided by applying a heavy coating of plaster of Paris or whiting, by covering the walls and roof with a heavy coating of vaseline or cup grease over which is usually applied heavy manila paper, or by blowing down daily with compressed air while the ventilating system is operating. No highly flammable solvents should be used for cleaning. If naphtha or benzine be diluted with about 60% of carbon tetrachloride they may be used, as the danger is thereby reduced; kerosene may also be used.

Scrapings should be placed in covered metal receptacles and immediately disposed of.

72. Spray booths used in connection with the application of pyroxylin finishes shall be used for no other purpose.

NOTE: If this caution is not observed, serious results are probable, for the

reason that alternating deposits of pyroxylin materials with varnish, oil base stains, ground coats, etc., make probable spontaneous heating and eventual ignition.

73. The amount of stock in spraying rooms shall be minimized to avoid unnecessary loss, care being taken to keep stock, especially that which has just been coated, well removed from the booth.



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It is obvious that a complete bibliography of the varied chemical domains so closely connected with the pyroxylin industries as to necessitate their consideration in this volume would be extremely cumbersome. Pyroxylin, oils, solvents, pigments, resins and plasticisers cover such a wide range a thorough listing of the literature would be almost a résumé of industrial chemistry. It seems more advisable, therefore, to limit the list of references to those which in the writer's judgment are of the most value to a reader who may be desirous of more detailed information than is available in this book.

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